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CHEMICAL VAPOR DISPOSITION

by

Battelle Memorial Institute

to

OFFICE OF THE DIRECTOR OF DEFENSE
RESEARCH AND ENGINEERING

FOREWORD

The material contained in these papers was presented originally at Battelle Memorial Institute on November 29, 1961, before an invited group representing industrial organizations currently or potentially interested in chemical vapor deposition as an industrial processing technique.

Since the information covered is of general interest at the present time, the material has been slightly revised and is being given further distribution as a DMIC report.

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THE PROMISE AND PROBLEMS OF CHEMICAL
VAPOR DEPOSITION

by

J. M. Blocher, Jr.

Chemical vapor deposition is making a significant impact on our economy at present and premises to be of greater importance in the future. In this presentation, I should like to compare chemical vapor deposition with the better known kindred processes, electrodeposition and vacuum metallizing, and to indicate several areas of current or impending commercial use. We shall find problems and limitations along the way, limitations imposed in many cases by our lack of fundamental knowledge of the process. However, we shall find much promise in these areas and others which may appear to be more "blue sky", but which deserve our consideration.

Chemical vapor deposition is one of the techniques which can aptly be termed "molecular forming", that is, building up of coatings, or massive deposits, by deposition of molecular or atomic particles. In the case of electrodeposition, one of the molecular-forming pr   ses which has found wide commercial application, atoms of elements, or molecules of compounds, are deposited on a conducting surface by discharge of ions which arrive at the surface through a liquid medium.

Another of these molecular-forming processes is vacuum metallizing, a form of physical vapor deposition. This has also found wide commercial acceptance. Here, the medium is a vacuum, and the coatings are formed by condensation of a vapor of atoms or molecules of the coating material.

In chemical vapor deposition a solid product is formed, again in molecular or atomic steps. The reaction of a suitable vapor compound is made to occur on a heated surface. Pyrolytic carbon formed by thermal decomposition of hydrocarbons is an example. In some cases, the product forms as a "snow" from the vapor phase, for example in the preparation of TiO_2 pigment by the oxidation of $TiCl_4$. The chemical reaction used is one in which all of the components of the system except the desired solid product are volatile at the processing temperature. Table 1 gives examples of reactions used to apply ceramic coatings.

Molecular-forming processes have in common the potential of yielding dense deposits of controlled thickness and orientation. Each has its advantages and limitations. However, when these are analyzed (see Table 2), chemical vapor deposition comes out quite well by comparison. A large body of art and some science have been accumulated in the past 50 years.[1]*

Chemical vapor deposition is capable of yielding the greatest variety of products at rates of deposition equivalent to or exceeding those of electrodeposition and vacuum metallizing. It has the greatest throwing power of the three techniques. In view of this, one is compelled to ask the question, "Why then is the process not much more widely used?"

The fact that the substrate must usually be heated is a relative disadvantage. However, this is no longer a limitation in many cases of current and future interest where the substrate will be used at high temperatures.

*References are listed at the end of each section.

TABLE 1. TYPICAL CHEMICAL VAPOR-DEPOSITION
REACTIONS FOR CERAMIC COATINGS

$$Al_2Cl_6(g) + 3H_2O(g) = Al_2O_3(s) + 6HCl(g)$$

$$Al_2Cl_6(g) + 3CO_2(g) + 3H_2(g) = Al_2O_3(s) + 6HCl(g) + 3CO(g)$$

$$BeCl_2(g) + H_2O(g) = BeO(s) + 2HCl(g)$$

$$BeCl_2(g) + CO_2(g) + H_2(g) = BeO(s) + 2HCl(g) + CO(g)$$

$$MgI_2(g) + H_2O(g) = MgO(s) + 2HI(g)$$

$$ZrCl_4(g) + 2H_2O(g) = ZrO_2(s) + 4HCl(g)$$

$$2YCl_3(g) + 3H_2O(g) = Y_2O_3(s) + 6HCl(g)$$

$$2CrOCl_2(g) + H_2O(g) + H_2(g) = Cr_2O_3(s) + 4HCl(g)$$

$$CH_4(g) = C(s) + 2H_2(g)$$

$$C_2H_2(g) = 2C(s) + H_2(g)$$
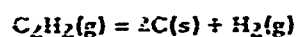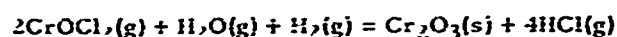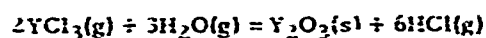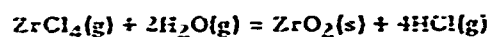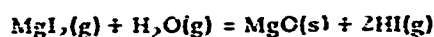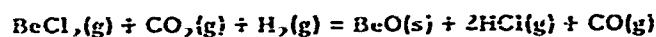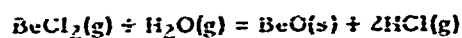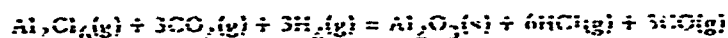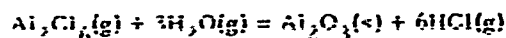
The relatively higher cost of the feed compounds has been a factor in the past in discouraging the use of chemical vapor deposition. However, the cost of these materials has dropped, as techniques for their production in increasing quantity have been developed.

The cost of feed materials and the fact that the substrate must be heated will always place some limit on this technique and make the use of the other molecular-forming processes more practical or economical in many cases. On the other hand, there are areas in which additional research and development will make chemical vapor deposition competitive. Finally, there is an increasing demand for coatings and products that can be obtained only by chemical vapor deposition. Our ability to apply this technique will most certainly increase with the development of fundamental information.

Let us consider some of the current and anticipated uses, to determine where the problems lie and what benefits may be derived from the development of additional fundamental information through research.

High-Purity Metal Production

The production of high-purity metals is an area in which chemical vapor deposition has been very effective, although with limited commercial impact until recently. Now all of the high-purity silicon going into semiconductor devices is prepared by this process. The effectiveness of the process stems from our ability to purify easily the volatile feed materials used. The phase change from the gaseous to the solid state during deposition is in itself a purification step. In the case of high-purity chromium, for example, products with only a few parts per million of residual impurities can be obtained.

TABLE 2. COMPARISON OF MOLECULAR FORMING PROCESSES

Factor	Electrodeposition	Vacuum Metallizing	Chemical Vapor Deposition
Feed	Ionic solution	Product vapor	Compound vapor (halide, carbonyl, metal-organic)
Method of activation	Ion discharge	Dissipation of ΔH_v	Supply of ΔE_{net}
Temperature	25 to 100 C. (aqueous) >300 C. (fused salt)	Boiler, 250 to 2000 C. substrate, room temperature	Substrate, 150 to 2000 C.
Typical rate for continuous films	0.3 to 10 mil./hr.	1 to 10 mil./hr.	1 to 20 mil./hr.
Throwing power	Fair	Poor	Good
Uses	Refining, forming, decorative, protective coatings	Decorative coatings, electronic films	Refining, forming, decorative and protective coatings, electronic films
Products	Li, Na, K, Rb, Cs, Cu, Ag, Au, Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, B, Al, Ga, In, Tl, Ti, Zr, Hf, Cb, Ta, As, Sb, Bi, Cr, Se, Te, Mn, Re, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, rare-earth metals and a few alloys	All solid elements (C, Ta, W, with difficulty); most halide salts and other thermally stable compounds	All electrodeposited metals except alkali metals, alkaline-earth metals, Ag and Au (with difficulty) Plus: C, Si, Th, V, Mo, W, U, metal carbides, nitrides, silicides borides, oxides, sulfides, selenides, tellurides, intermetallic compounds and alloys

Van Arkel and de Boer[2] in their work with the iodide process, used a hot filament as a deposition surface for titanium, zirconium, and other metals. This has the effect of avoiding contact of the product with the container. Attention to the mechanism of growth on the filament and the crystal morphology can yield a product in the form of a dense bar which, in the case of metals, can be directly worked. However, there is limited interest in controlling the form of the deposit to permit direct working, because other shapes are usually desired, often as alloys obtained by melting. (Incidentally, many alloys can be formed by codeposition from mixed feed vapors.)

More important is the problem of mass and heat transfer. It is difficult to get efficient conversion of the feed material with the limited surface area provided by a filament bundle. A fluidized bed of seed particles can be used to provide the large area required for efficient mass transfer. As discussed in the final paper, there is much to be learned regarding mass and heat transfer in both filament bundles and fluidized beds.

It is believed that the production of columbium by the hydrogen reduction of columbium pentachloride in a fluidized bed of seed particles will be the first significant commercial application of this type.

Coating of Particles

Chemical vapor deposition in a fluidized or otherwise agitated bed of nuclear fuel particles is effective in providing them with fission-product retentive coatings or reaction barriers. Typical coatings are shown in Figures 1 and 2. Interest in this field is steadily increasing, and the use of coated fuel particles is already planned for the cores of several nuclear reactors.

Here, efficient mass transfer is again a factor, but the crystal morphology is also of prime importance. For fission-product retention, a fully dense coating is desirable. How is this attainable? Among other factors influencing the quality of the coating, there is evidence that the effect of particle-to-particle collision on the nucleation and growth of the coating is beneficial.

This effect of mechanical impingement has been observed at Battelle and in other laboratories doing fluidized-bed coating work. Deposits of columbium on thermocouple wells partially exposed to particle bombardment are rough and grossly crystalline in the unexposed area, whereas the area subjected to bombardment is polished and microcrystalline. Several possible explanations can be devised. Because of its importance in fluidized-bed coating, the mechanism should be identified.

Molecular Electronics

One of the most significant applications of chemical vapor deposition is in the field of molecular electronics which promises even further reduction in size of our electronic "black boxes". Here, epitaxially grown semiconductors and resistive, conductive, and insulating films are of interest. Here also, the mechanism of crystal nucleation and growth is of paramount importance.
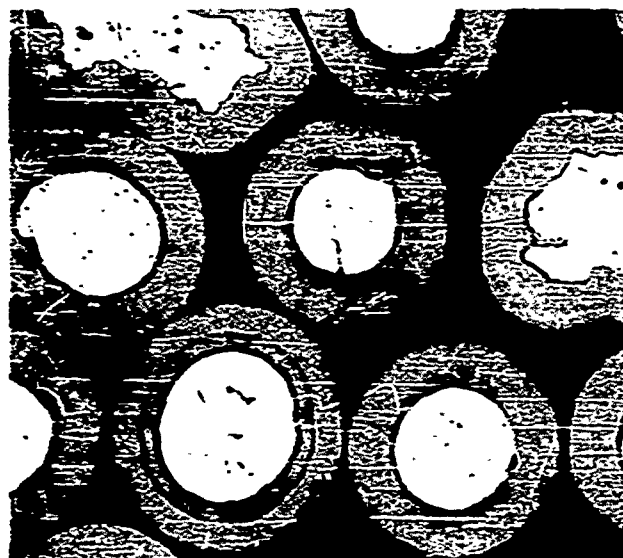
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FIGURE 1. 125-μ UC_2 COATED WITH PYROLYTIC CARBON
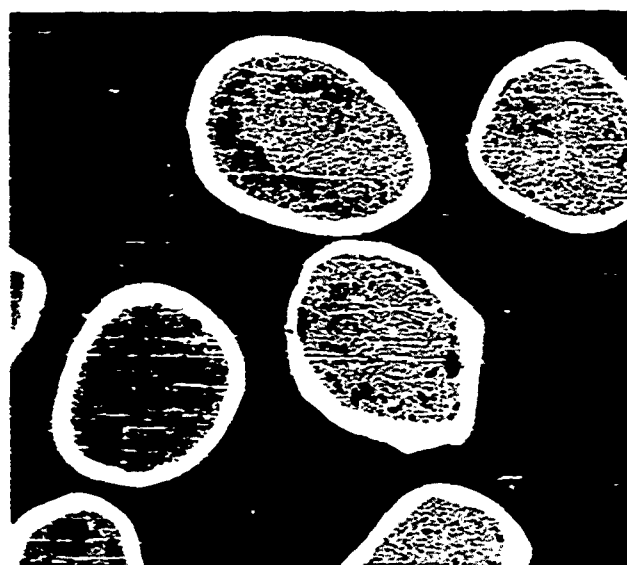
N59016

FIGURE 2. 125-μ UO_2 COATED WITH TUNGSTEN

Questions such as the following arise: To what extent does migration of surface-adsorbed species occur before incorporation of the product atoms into the structure? What are the migrating species - atoms of the final product, or intermediates in the over-all deposition reaction? What is the role of substrate surface condition? Increased knowledge in these areas will certainly be of value in stimulating progress.

Refractory Metal Coatings

Chemical vapor deposition is uniquely applicable to the formation of coatings of the refractory metals: columbium, molybdenum, tantalum, and tungsten. These cannot be electrodeposited from aqueous solution, and the very high temperatures required for their vaporization makes the use of vacuum metallizing unattractive. Tungsten coatings obtained by hydrogen reduction of tungsten hexafluoride vapor at temperatures of from 400 to 600 C have shown considerable promise as liners for rocket nozzles and similar applications.[3,4] However, workers have recently become disenchanted with the approach in one instance because stresses set up by differential contraction of the tungsten and the substrate on cooling from deposition temperature have invariably resulted in rupture of the coating.

In this case, as in many others involving vapor-deposited coatings, the stress necessary to rupture the coatings is a fraction of the normal tensile strength of the particular material involved. This is explained by the fact that most coatings of this type show grain growth radially from the surface, with varying degrees of "fit" between grains. At some stress below the yield strength of the material, a pseudo-brittle fracture occurs by separation between weakly bonded grains. Although it remains to be proven, rejection of impurities to the surface of adjacent grains during growth may be a factor in poor intergranular strength.

A full understanding of the mechanisms of crystal nucleation and growth and the mechanism of impurity deposition is of obvious importance if this situation is ever to be altered.

Corrosion-Resistant Coatings

Another application of chemical vapor deposition of growing importance is the coating of refractory metals and other materials for oxidation or corrosion resistance. Chromizing, aluminizing, and siliconizing have all given useful diffusion coatings.

These coatings are frequently applied by a pack-cementation process of the type discussed in the fifth paper. Here, the article to be coated is packed in powder of the coating material plus an ammonium halide, for example, to form volatile halides of the coating material. Although these coatings are basically protective, failure by localized defects has limited their utility. This is an even greater problem with vapor-deposited "overlay" coatings where little or no interdiffusion with the substrate occurs. Here, we must rely upon continuity of the coating, and all that this entails in terms of intergranular "fit" and intergranular strength. Further, the adherence of overlay coatings often is poor since a diffusion bond is not formed.

Again, we need a full understanding of the crystal nucleation and growth involved. The long-term payoff will be our ability to tailor these processes to yield a more desirable product.

Pyrolytic Carbon

Pyrolytic carbon is by definition the product of chemical vapor deposition. Its anisotropy with respect to thermal conductivity has excited the imagination of those designing nose cones, rocket nozzles, and leading edges. Here is a material — apparently made to order — with low thermal conductivity perpendicular to the surface and high thermal conductivity parallel to the surface. Unfortunately, pyrolytic carbon is also anisotropic with respect to thermal expansion. This leads to internal stress as the article is cooled below the temperature of deposition and delamination can occur. We have not encountered problems with delamination in coating spheroidal nuclear fuel particles with pyrolytic carbon, such as those in Figure 1. However, it is a distinct problem with irregular shapes.

Because of widespread interest in pyrolytic carbon and intensive support, much work of a fundamental nature has been done on this process. However, there is still much to learn.

In some cases, carbon deposition occurs where it is not desired. This is very troublesome in preparing metal coatings by thermal decomposition of metal-organic compounds. A better understanding of the mechanism of carbon codeposition should help in the elimination of this difficulty.

Refractory Carbides

Another useful aspect of chemical vapor-deposition processes is the ability to control what goes on in the solid phase by proper attention to the thermodynamic activity of components of the vapor phase. This principle has been used at Battelle to facilitate the coating of graphite tubes with carbides of columbium, tantalum, and zirconium.[5] It was possible to apply uniform coatings to the inside wall of tubes having length-to-bore-diameter ratios of up to 450.

Now, the carbides themselves can be obtained by conventional chemical vapor-deposition procedures, such as (1) deposition of a metal to be later intradiffused with the carbon, or (2) simultaneously feeding a metal compound and a hydrocarbon. However, if these were applied to tube coating, nonuniform deposition would result, with the coating being thicker at the vapor entrance end of the tube.

The principle of the improved method can be understood by reference to Figure 3. This example shows the effect of pressure at a given temperature on the thermal decomposition of a columbium pentahalide vapor. At low pressures, the rate of collision of CbX_5 molecules with the surface is insufficient to offset evaporation of the metal, and a net loss of "chewing" occurs. As the pressure is raised, a null point is reached, followed by a region in which a deposit of columbium builds up on the heated surface. If only the reaction $CbX_5(g) \rightarrow Cb(s) + 5X(g)$ were involved, increase of the halide pressure

The graph shows Deposition Efficiency (+, 0, −) on the vertical axis versus Log Halide Pressure on the horizontal axis.

$$CbX_5(g) \rightarrow Cb(s) + 5X(g)$$

Deposition

Chewing

$$Cb(s) \rightarrow Cb(g)$$

$$CbX_5(g) + Cb(s) \rightarrow \genfrac{}{}{0pt}{}{CbX_2(g)}{CbX_3(g)}$$
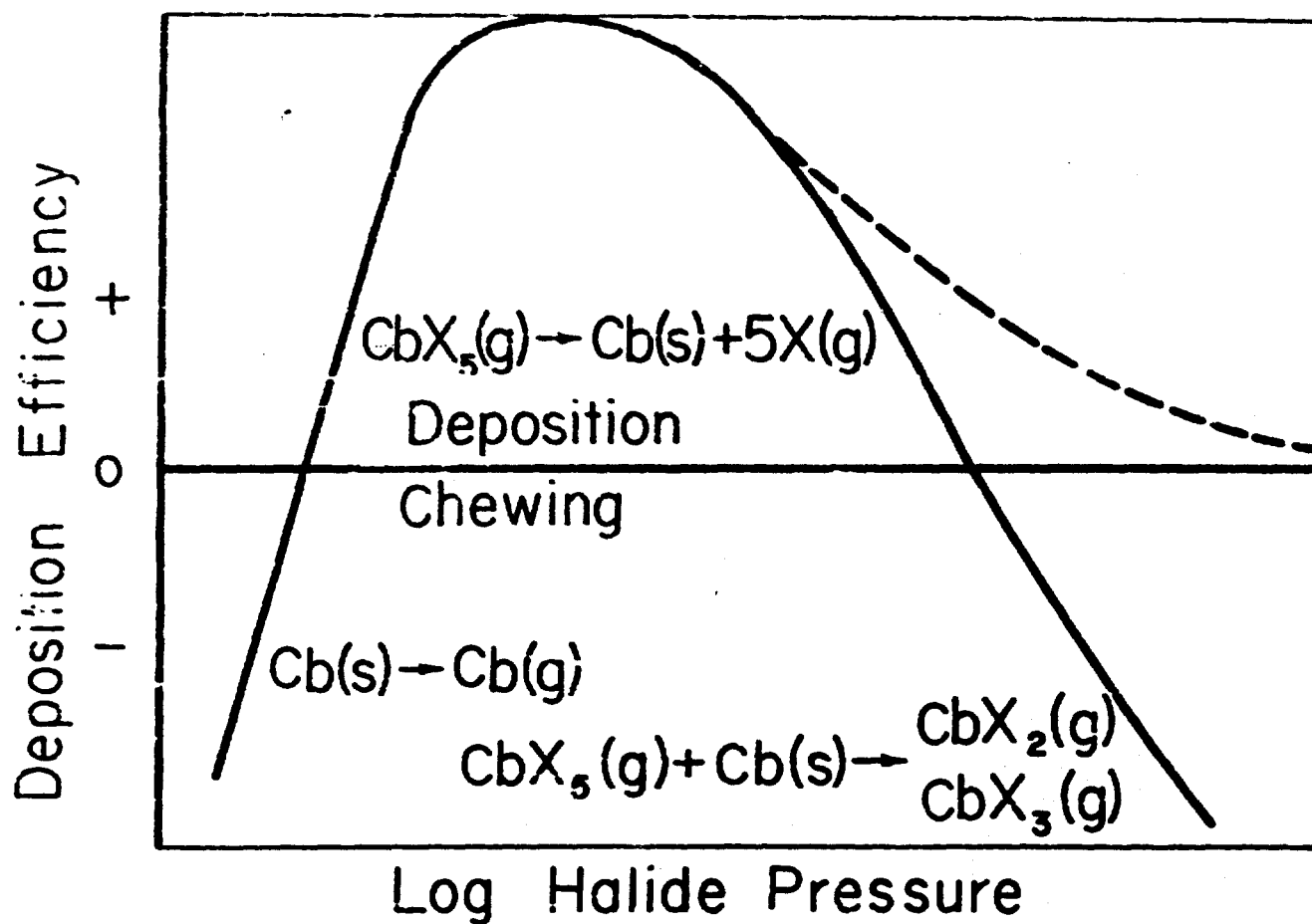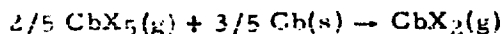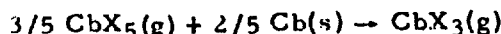
FIGURE 3. EFFECT OF HALIDE PRESSURE ON DEPOSITION EFFICIENCY

would asymptotically decrease the fraction of the halide decomposed to zero. However, if, as in this case, lower valent gaseous halides are stable, a second null point is reached, and chewing reactions such as

$$2/5 \, CbX_5(g) + 3/5 \, Cb(s) \rightarrow CbX_2(g)$$

or

$$3/5 \, CbX_5(g) + 2/5 \, Cb(s) \rightarrow CbX_3(g)$$

occur as the pressure is increased further. We have termed this null point a "limiting pressure for metal deposition". The same situation holds for reaction of carbon with the halide to form columbium carbide, except that the limiting pressure for carbide deposition is higher. In fact, it can be shown thermodynamically for the simplest case that, if the equilibrium vapor phase contains only one lower valent halide and monatomic halogen, the limiting pressures for metal and carbide deposition are related by the equation:

$$\log \frac{P_{MC}}{P_M} = \frac{-\Delta F_{MC}}{(n-1) \, 2.303 \, RT} \quad ,$$

where

P_{MC} = Limiting pressure for carbide formation

P_M = Limiting pressure for metal formation

ΔF_{MC} = Free energy of formation of the carbide MC

T = Temperature, K

R = Gas constant

n = Number of halogen atoms per atom of metal in the lower halide.

Practically, one determines the limiting pressure experimentally to give data of the type shown in Figure 4, and then operates in a pressure-temperature range where only the metal carbide can form. If the temperature is appropriately chosen, and the vapor-flow rate is sufficiently high, the rate of carbide formation can then be controlled, not by the vapor-phase mass-transport mechanisms involved in many chemical vapor-deposition processes, but by the rate of diffusion of carbon through the carbide coating. This results in a uniform coating, such as shown in Figure 5, along the entire length of the tube.

As an alternative to the pressure control described here, hydrogen reduction of the halide can be carried out at atmospheric pressure, and the thermodynamic activity of columbium in the vapor phase can be adjusted by the hydrogen/hydrogen-halide ratio in the feed vapor.

Further knowledge of the vapor species involved would greatly increase the applicability of this principle.
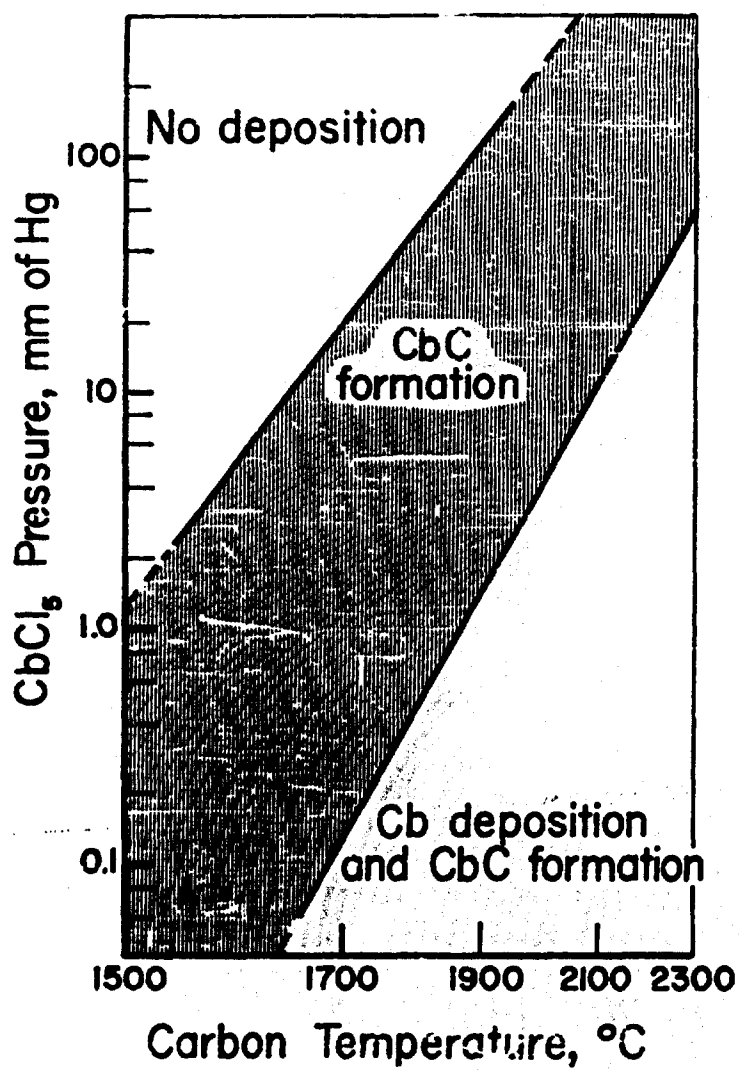
FIGURE 4.   RANGE OF CbC FORMATION IN REACTION $CbCl_5 + C = CbC + 5/2\ Cl_2$

N41101

FIGURE 5. 20-MIL CbC COATING ON ATJ GRAPHITE

Other Potential Applications

So much for the applications of chemical vapor deposition which are or soon will be commercial realities. Consider briefly the areas of future promise.

One of the intriguing applications is in the formation of composite materials. These can be formed as a dispersed second phase codeposited in a matrix, or by consolidation of powders of one material coated with another. In Figure 6 are compared a cermet made by pressure bonding mixed metal and ceramic powders and one prepared from the same ceramic particles, metal-coated by chemical vapor deposition in a fluidized bed of the particles.

In directly forming a massive two-phase deposit it should be possible, for many combinations of materials, to codeposit the second phase in a much finer dispersion than is obtained by normal ceramic techniques. For example, the alumina coatings we have prepared by hydrolysis of aluminum chloride vapor at 1000 C appear to be composed of microcrystalline α-alumina in a glassy matrix. They have the hardness and density of sapphire. Figure 7 shows alumina-coated particles of this type.

And now let us consider a somewhat more "blue-sky" example. What could be done if we really knew all there is to know about crystal nucleation and growth in chemical vapor deposition? I am convinced that we could devise methods of controlling grain orientation and size in such a way as to vapor form tungsten directly into large shapes having grain structure and properties similar to those of wrought tungsten.

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a. Metal-Coated Ceramic Powders
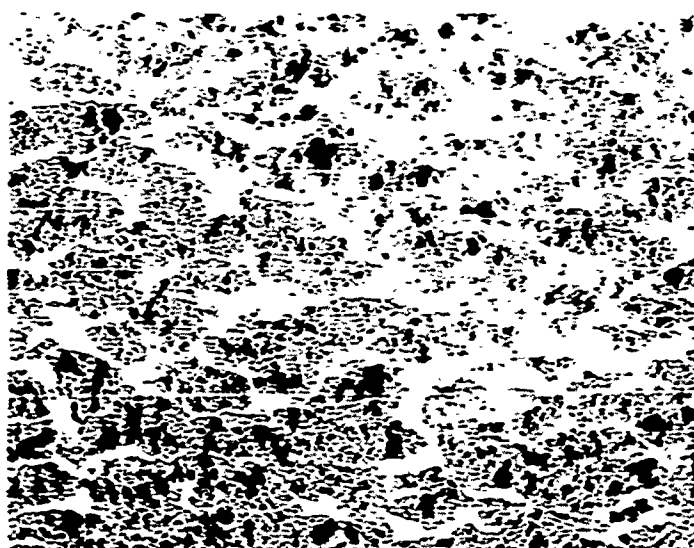
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b. Mixed Metal-Ceramic Powders

FIGURE 6. PRESSURE-BONDED CERMETS
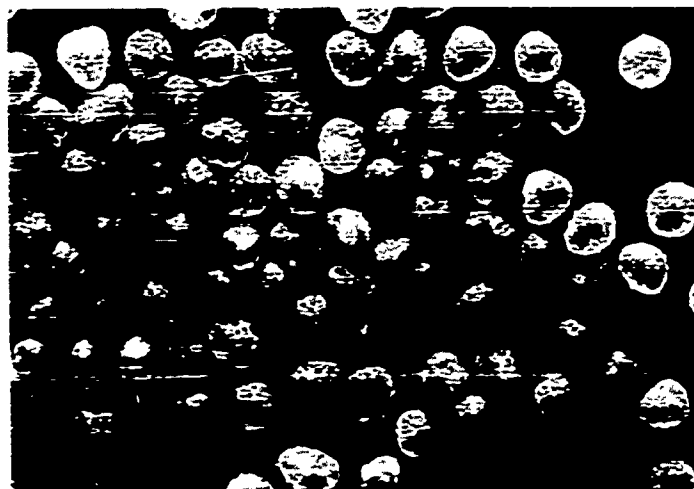
FIGURE 7.   125-μ UO$_2$ PARTICLES COATED WITH 45 μ OF α-ALUMINA

Summary

In summary, let me briefly review the areas in which fundamental research would be of value.

(1) Mechanisms of crystal nucleation

(2) Mechanisms of grain growth

(3) Mechanisms of impurity deposition

(4) The effect of mechanical impingement during deposition

(5) Mechanism of carbon (or oxygen) contamination in metal-organic or carbonyl decomposition

(6) Mass and heat transfer in systems of various configuration.

These are the areas in which fundamental research will lead to the solution of present problems and to new and profitable applications of chemical vapor deposition.

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THE GROWTH OF CRYSTALLINE FILMS AND LAYERS BY CHEMICAL VAPOR DEPOSITION

by

E. M. Sherwood and R. C. Himes

Introduction

Man has long been fascinated by matter in the crystalline state but only in recent decades has he begun to understand something of the true nature of the laws and forces governing its formation. An early crystallographer described crystalline form as "the external manifestation of internal order". The discovery of X-rays and the development of X-ray diffraction technique provided further convincing evidence of this internal order. Modern atomic and solid-state physics, together with the tools of spectroscopy, electron and neutron diffraction, electron microscopy, and special physical- and mechanical-property measurements, have added further impetus to the rapid growth of the body of knowledge concerning crystalline matter. While adequate means of evaluating the characteristics of crystalline materials thus are well known, less is known about such fundamental phenomena as the nucleation and growth of these still fascinating structures.

It is the purpose of this presentation first to describe briefly the role played by chemical vapor deposition in preparing high-purity material in a well-ordered state. Next, I shall present some illustrations of work in this field. Then a discussion will be given which, it is hoped, will indicate the potential of chemical vapor deposition as a means of arriving at a better understanding of matters such as how crystal growth begins and how it may be controlled. Finally, I shall suggest goals in this area which may be reached as a result of new knowledge developed when we know more about the fundamental aspects of chemical vapor deposition processes.

Bulk Deposits

The ordered nature of massive metal laid down by chemical vapor deposition is manifest in the very name applied to such deposits formed on hot wires, i. e., "crystal bar". Figure 1 shows a short section of a 3/4-inch-diameter titanium crystal bar that exhibits large grain structure. These deposits often are laid down at temperatures sufficiently elevated to permit the growth of large crystals which may cover the whole cross section of the bar. In Figure 2, a portion of a 1/4-inch-diameter titanium crystal bar, formed at a temperature very close to the melting point, is shown, on the external surface of which only three major grain boundaries appear.

One metallographic technique often used to develop information regarding the orientation and crystalline perfection of individual grains in a crystalline material is
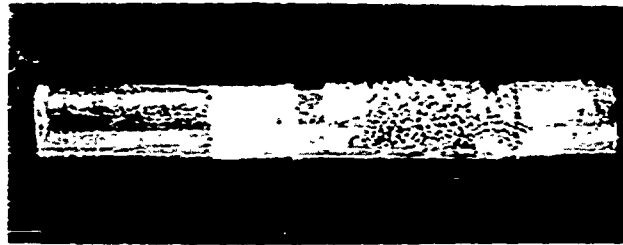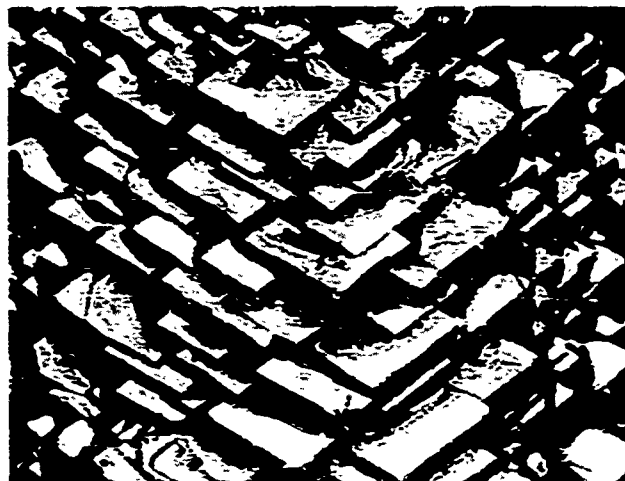
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FIGURE 1. SECTION OF 3/4-INCH-DIAMETER TITANIUM CRYSTAL BAR

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FIGURE 2. SECTION OF 1/4-INCH-DIAMETER TITANIUM CRYSTAL BAR
DEPOSITED AT A TEMPERATURE NEAR THE MELTING POINT

N84810

FIGURE 3. GROWTH STRUCTURE ON CRYSTAL BAR OF FIGURE 1

that of deep etching to form what are called etch pits. Chemical vapor-deposition techniques have been used in several ways to provide similar information. For example, etch pits have been formed on germanium single crystals by attack with iodine vapor.[1] Inversely, the growth habits of metal crystals formed by chemical vapor deposition can be studied. Figure 3 shows a portion of one grain of the crystal bar of Figure 1 at higher magnification and indicates a growth habit that is quite different from those of its neighbors. The study of such structures should be particularly rewarding.

Under some conditions, crystals with several well-developed faces may result, as is illustrated by the iodide chromium deposit of Figure 4. Such metal contains less than 10 ppm of any single metallic impurity. On close inspection, growth steps can be discerned on two of the faces of the crystal shown in Figure 4. We shall have more to say about these later. The growth habit of rapidly deposited GaAs is shown in Figure 5. Another chromium crystal is seen in Figure 6. Here the growth steps are quite well developed. Let us now look at such a crystal at a higher magnification (Figure 7) in which the ordered nature of the growth pattern is even more apparent.

Figure 7 also illustrates how crystals can be used to study the mode of deformation of high-purity metals when subjected to external forces. Striations which run in a different direction than do the growth steps can be discerned. These are slip lines which were developed when this chromium crystal was subjected to compressive forces. The final illustration in this series, Figure 8, is an electron micrograph of a deformed chromium crystal depicting both growth steps and slip lines. Of further interest are the numerous small nodules everywhere present on the surface shown in Figure 8. Their true nature is not known although it is postulated that they could be minute oxide crystals. The growth features illustrated above all are of a "macro" nature. A discussion of atomic-scale growth steps is presented in the third paper of this series.

For some materials, many small crystals form which grow more or less independently, thus yielding a loosely knit body of poor mechanical strength. An example of this is thorium crystal bar, a cross section of which is shown in Figure 9.

While we know in a general way some of the reasons why these massive deposits form as they do, we do not know how to control or to modify them to any great extent. It is hoped that future fundamental research will supply much of this missing information and, hence, enable us to provide new forms of these and other materials potentially useful in, as yet unspecified, industrial applications.
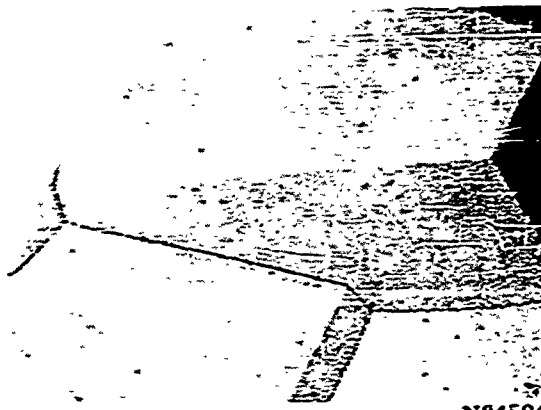
Thin-Film Deposits and Epitaxial Growth

In recent years, workers in the field of electronics technology have devoted much effort toward miniaturization of devices and components. An important concept thus developed is that of multilayer solid-state circuits. In such circuits, thin films of appropriate materials are successively deposited one over the other through special masks to form a composite structure containing resistors, inductors, capacitors, insulators, heaters, and the conductors required to properly connect these components. Figure 10 illustrates schematically one of a number of ways in which a multilayer,
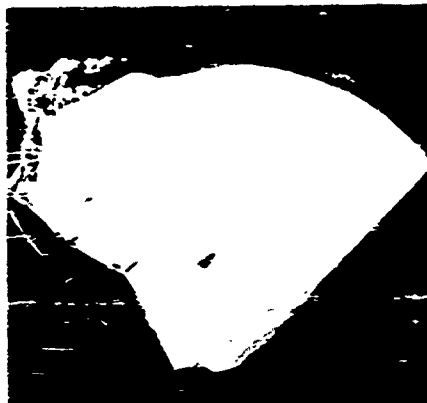
N84809   50X   N84594

FIGURE 4. IODIDE CHROMIUM   FIGURE 5. GROWTH HABIT OF RAPIDLY
CRYSTAL SHOWING WELL-   DEPOSITED GALLIUM ARSENIDE
DEVELOPED FACES

25X   N84534   800X   N84535

FIGURE 6. LIGHT MICROGRAPH   FIGURE 7. LIGHT MICROGRAPH SHOWING
OF (111) FACE OF A STRAINED   SURFACE OF (111) FACE OF A MECHANI-
IODIDE-CHROMIUM CRYSTAL   CALLY STRAINED IODIDE CHROMIUM
SHOWING GROWTH STEPS   CRYSTAL

15.000X N84536
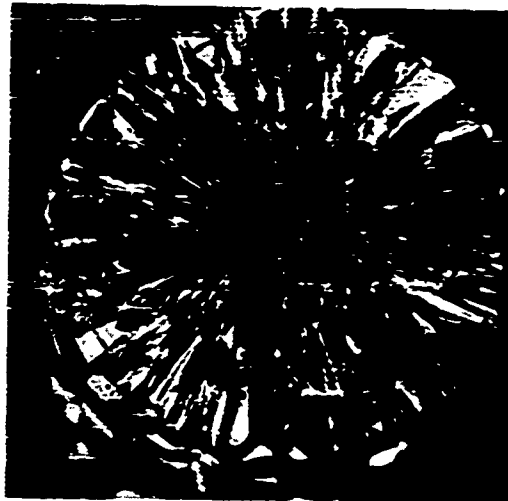
N31246

FIGURE 8. ELECTRON MICROGRAPH
OF (111) FACE OF A STRAINED IODIDE
CHROMIUM CRYSTAL

FIGURE 9. CROSS SECTION OF 3/16-
INCH-DIAMETER THORIUM CRYSTAL
BAR

Positive Formvar Replica Shadowed with
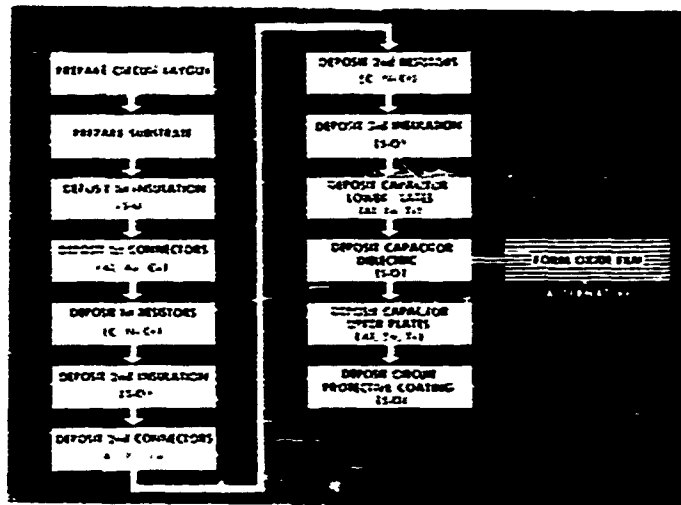Platinum at Arc Tan 5.

FIGURE 10. SEQUENCE OF OPERATIONS: MULTILAYER THIN-FILM CIRCUIT

thin-film electronic circuit may be constructed. The circuit example shown in
Figure 10 contains only passive components. In practice, active components, such as
transistors and photosensors, would be included. Such active components also can be
fabricated by chemical vapor-deposition techniques.[2] Some of the challenging
problems we have encountered in this area will be mentioned later.

The term "thin", used in this discussion, refers to films ranging in thickness
from 10^{-7} cm (or 10 angstroms, a distance equal to about twice the interatomic dis-
tance in most solids) to 10^{-2} cm (0.004 inch).

While a number of the desired thin-film materials can be deposited by vacuum
evaporation (actually, the process should be described as condensation of evaporated
atoms on a substrate), other materials can be handled best by chemical vapor
deposition.

Before discussing the application of chemical vapor deposition to the growth of
thin films, consideration must be given to an important and sometimes uncontrollable
factor which must be taken into account in thin-film technology. This factor involves
the structure of the substrate on which the film is laid down and how it influences the
structure of the deposited film.

Many years ago, it was observed that thin gold films deposited on single crystals
of rock salt were likewise single crystals; also, polycrystalline films were formed on
polycrystalline substrates. Naturally, a name had to be invented for this phenomenon,
since scientists are obsessed by a desire to carefully name any observable effect even
though they do not understand it very well. Thus arose the term epitaxy[3], which
refers, not to an exotic means of transportation, but rather to an arrangement of
deposited atoms on a substrate. Epitaxial growth comes about as a result of an atomic
interaction between the substrate and the deposit which, under suitable conditions, can
exert a directive influence on the nature and orientation of the deposit. However,
neither the crystal structure nor the lattice constant of the deposit and the substrate
need be the same. Rather, epitaxy is determined by the relations between (1) the
geometry of the atomic arrangement in the exposed face of the substrate and (2) that of
the atoms in the appropriate face of the depositing material.

At present, most of our knowledge about crystalline thin films is based on
observations made on films formed by condensation.[4] The earliest observable stage
of growth is the formation of discrete nuclei when the total amount of the deposit, if
uniformly distributed over the deposition surface, is as yet insufficient to form a
monatomic layer. No direct evidence is available to explain how this initial nucleation
occurs. Better experimental technique is needed to discover the details of this proc-
ess. Nuclei as small as 10 A in diameter, probably consisting of about 50 atoms, can
be observed by electron microscopy. After such stationary nuclei are formed on the
substrate surface, direct evidence indicates that the lattice spacing is that of the de-
posited material in bulk, not that of the substrate. However, the state of strain existing
at the deposit-substrate interface is unknown and may exert an important influence on
the character of the deposit.

Recent work with the field-emission microscope[5] has permitted continuous observation of the adsorption, migration, and aggregation of silver on tungsten and molybdenum, as well as the adsorption and desorption of residual gases. Nucleation was observed to occur much more readily on areas of a tungsten single crystal containing many steps and kink sites, than on relatively smooth crystal planes. Even at 200 K, the condensed silver atoms are highly mobile in preferred crystalline directions.

For a sufficiently large number of nuclei, further deposition gives rise to growth by (1) direct deposition on existing nuclei, (2) an interchange of atoms between neighboring nuclei in which large nuclei grow at the expense of small ones, and (3) physical growing together of neighboring deposits. In cases for which growth of nuclei normal to the substrate is favored, quite large isolated crystallites can result as we have seen in the cases of some iodide metals illustrated previously.

The practical applications of thin films generally make use of properties which are structure sensitive. Therefore, careful control of the structure is mandatory.

A study of nucleation under various conditions of deposition and on substrates of differing nature (amorphous, crystalline, atomically rough or smooth) is essential to an understanding of the physical properties of films.

It seems probable from accumulating evidence that the structure of very thin deposited films depends to a large extent on the mobility of the deposited particles.[6] In the case of very clean substrates, such mobility is in turn controlled by potential barriers due to the atomic structure of the substrate surface.

Perhaps the earliest example of the formation of epitaxial deposits utilizing the methods of chemical vapor deposition was the work reported by Koref[7] in 1922. He showed that the diameter of a single-crystal tungsten wire, made by the Pintsch temperature-gradient process, could be increased several times by heating it at a suitably high temperature in a hydrogen/tungsten hexachloride atmosphere. Not only was the finished deposit a single crystal, but also the initial cross-sectional shape of the wire was maintained.

In the past 2 years, as a result of considerable pressure to produce solid-state devices largely for military application, high-quality epitaxially grown films and massive deposits have been made using chemical vapor deposition.

Efforts in this area have been concerned primarily with the epitaxial growth[8] of crystals of the Group IV elements, germanium and silicon. As a result, in the case of these two elements at least, reasonably adequate understanding of some aspects of the over-all process has been obtained. Application has been reported of both the closed-cycle van Arkel/de Boer technique, with iodine as the carrier in a disproportionation reaction, and with the continuous-flow process, in which either an inert gas sweeps volatilized halide compound past the deposition surface, or in which hydrogen, employed in a halide-reduction reaction, serves as the carrier.[4, 9, 11] For these reactions, species present in the vapor have been identified, and the chemical equilibria affecting the deposition process have been studied. Some understanding has been obtained of the dependence of crystal-growth rate and of the character of the crystalline

deposit on variables such as relative and total concentrations of vapor species, temperatures and temperature gradients, growth direction (i. e., crystalline orientation), substrate type, and substrate or seed-crystal condition.

Needs in this area include better control of thickness and uniformity of deposits as well as of the degree of crystalline perfection. In addition, we should know more about substrate preparation and pre-treatment and control of electronically active, deliberately introduced impurities ("doping" agents).

A study of epitaxial deposits formed in laboratory investigations carried out at Battelle indicates the presence of controlling factors whose exact role is not understood.

For illustration, consider the following examples. Figure 11 is a photomicrograph of a GaAs deposit on a mechanically polished GaAs substrate. The deposit is shown at an early stage, illustrating identically oriented crystal plates grown from scattered nuclei. The apparent scratches on the substrate were not observed before the deposition was performed but were developed in the course of the deposition. Compare this with Figure 12 which shows the geometry of a deposit laid down under exactly similar conditions on a chemically etched GaAs substrate. Here islands of substrate protrude through the overgrowth

Those of you familiar with the III-V semiconductors are aware of the interesting differences between the (111) and ($1\bar{1}\bar{1}$) faces of these zinc blende structures. Differences in the chemistry of these faces and in crystal growth in the two directions are manifest in the nature of deposits on the two faces. Figure 13 shows the rough, highly oriented growth obtained on the face terminating in gallium. In contrast, Figure 14 shows the smooth, layered, monolithic growth obtained under similar conditions on the arsenic face. The opportunity to investigate these phenomena and the chemical influences of the substrate surfaces upon the various steps in the growth process makes this a very attractive area for research.

The influence of impurities on epitaxial deposits is another area in which unrelated observations suggest unexplained phenomena and possibly profound relationships. Impurities have been seen to exert directive influences on morphology of deposits. For example, the shape of vapor-grown ZnS crystals can be greatly altered by additions such as copper. Stabilization of the cubic phase at high temperatures by impurities has also been reported. In semiconductors, of course, impurities are of paramount importance. A few studies have been made in which particular attention has been paid to the transport of impurities from source materials to deposit. In some experiments, proportionate transport was observed. In others, p-type deposits were grown from n-type source material. These observations, though not necessarily contradictory, do point to the need for further investigation. It is significant that problems in all of these areas can be related to the mechanisms of nucleation and crystal growth, which are themselves yet to be fully understood.

In regard to epitaxial growth of crystals of elements (other than germanium and silicon) and of compounds, the state of the art is far less advanced. Some exploratory work has been done with potentially important binary compounds such as GaAs and GaP, using halogen transport similar to that discussed above. The precise chemical reactions occurring have not been determined with certainty and, consequently, adequate
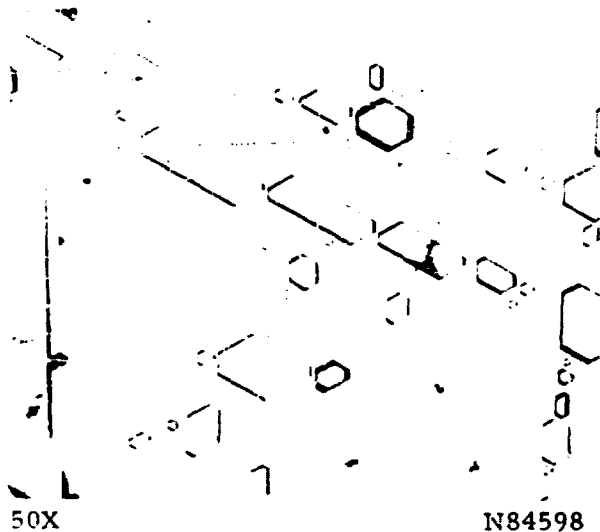
50X   N84598
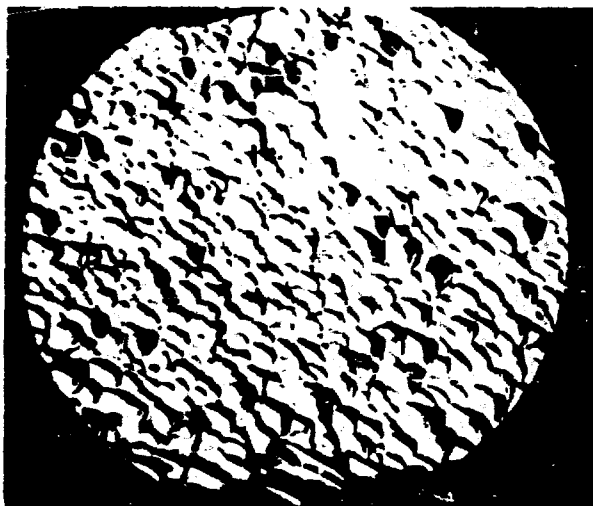
FIGURE 11. GALLIUM ARSENIDE
DEPOSIT ON MECHANICALLY
POLISHED GALLIUM ARSENIDE
SUBSTRATE
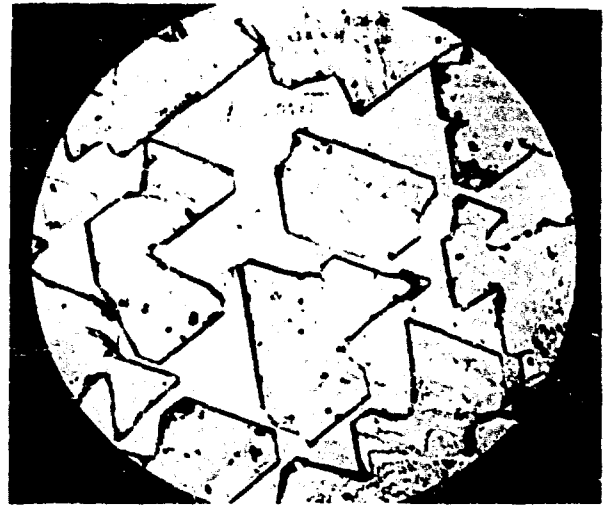
75X   N84595
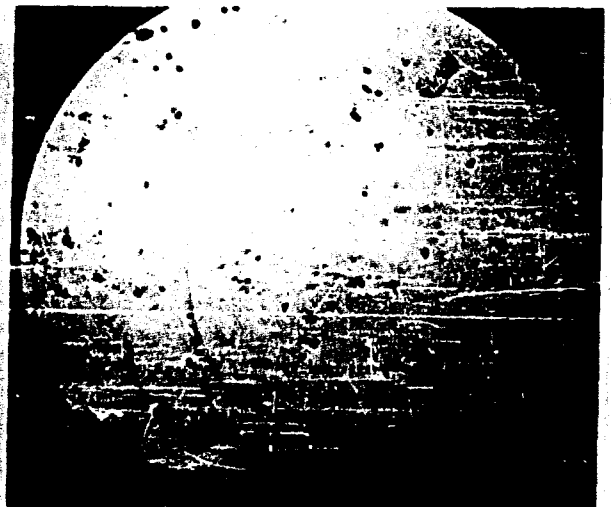
FIGURE 12. GALLIUM ARSENIDE
DEPOSIT ON CHEMICALLY ETCHED
GALLIUM ARSENIDE SUBSTRATE

75X   N84597

FIGURE 13. GALLIUM ARSENIDE
CRYSTAL: (111) FACE TERMINATING
IN GALLIUM

75X   N84596

FIGURE 14. GALLIUM ARSENIDE
CRYSTAL: (111) FACE TERMINATING
IN ARSENIC

understanding of the chemical equilibria, necessary for control of the processes, has not yet been developed. In the case of compounds, the over-all crystal growth process is obviously more complex than that for elements. More species are present in the vapor system, and analysis and control of vapor equilibria and vapor transport will be more difficult. The crystal formation step also is more complex since it involves the incorporation of two types of atoms into the crystal lattice. The effect of crystalline orientation on growth rate and product quality likewise may be more pronounced because of polarity effects.

The mechanism of epitaxial growth of crystals of metallic elements by chemical vapor deposition, which appears to have received little attention to date, may be unique. Chemical bonding in the solid is different (i.e., it is metallic) than that in the classes of materials discussed so far. Also, the rate of migration of atoms on the crystal surface will be different and may proceed by a different mechanism.

It is important to note that in vacuum evaporation, conditions at the substrate may be far from those of equilibrium, particularly when the substrate is not heated appreciably. For chemical vapor deposition, in which the substrate must be heated, conditions much more nearly approaching those of equilibrium can prevail, with the result that single-crystal deposits, grown epitaxially by chemical vapor deposition, often resemble those of high perfection grown from the melt by allowing material to solidify on a seed crystal which is slowly withdrawn as freezing takes place. Vacuum-evaporated, single-crystal epitaxial deposits, on the other hand, may contain a greater number of dislocations than do melt-grown single crystals.

Another advantageous feature of the chemical vapor-deposition process is its active chemical nature, which in some cases permits cleanup of substrate surface impurities, such as oxides, prior to deposition.

Finally, chemical vapor-deposition processing potentially affords a much easier controlled introduction of doping agents than do other methods of deposition. Full understanding and utilization of this aspect of the process should permit future workers to achieve the extreme miniaturization and reliability which is the objective of the truly advanced concept of molecular electronic building blocks which can perform whole circuit functions.

Because of the demands of solid-state-device technology for immediately useful components, there has been even less opportunity for a fundamental study of the nucleation and growth of epitaxial deposits formed by chemical vapor deposition than for that accorded to vacuum evaporated deposits. As has been pointed out, our knowledge in this field leaves much to the imagination. Therefore, a research area with many attractive possibilities remains to be explored.

General Conclusions and Goals

It is believed that a more complete understanding of the fundamental parameters governing chemical vapor-deposition processes would permit reliable prediction of the nature of deposits which can be formed under sufficiently well-controlled conditions. Further, it should be possible not only to control these reactions but also to modify the

character of vapor-grown deposits without having to accept "what comes naturally". Such undesirable results as the formation of massive deposits which consist of long columnar grains grown normal to a deposition surface and which therefore exhibit low tensile strength in a direction parallel to the deposition surface may be avoided. Even today investigations dealing with pyrolytic carbon are in progress which are aimed at influencing a growth habit of this type so as to secure improved heat-transfer characteristics for important end uses.

I shall now suggest some specific goals in the areas under discussion which may be reached if a better understanding of chemical vapor deposition processes can be developed.

(1) Preparation of large single crystals of various useful materials having selected orientation and containing a minimum of dislocations

(2) Formation of massive deposits of polycrystalline metals, alloys, intermetallic compounds, and refractory compounds of metals in a fully consolidated form and in useful shapes

(3) Preparation of substantially dislocation-free epitaxial thin films and layers, of controlled composition and dimensions, for use in thin-film and molecular electronic applications

(4) Development of new crystalline forms of matter for use as protective coatings or as materials of construction in environments which no currently available materials will tolerate.

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THE SCIENCE OF WHISKER GROWTH

by

E. E. Underwood and C. F. Powell

Small, elongated crystals, of metals, nonmetals, or compounds, are called whiskers. Whiskers have been known for several centuries, but modern interest in them stems from about the last decade.[1] Their potentially great strengths, approaching the theoretical limit, offer the greatest inducement to commercial exploitation. Interest in their magnetic and semiconductor properties also runs high. In the preceding section, mention was made of crystals essentially two or three dimensional in nature. I would like to talk about the one-dimensional aspects of crystal growth (specifically whiskers), and mostly about recent developments based on dislocation theory. Dislocations, as you know, are merely the result of atomic deviations from perfect periodicity of the crystal lattice.

Whiskers can be characterized to some extent in terms of their physical properties. They occur in a variety of sizes and shapes, normally having diameters of 1 to 50 microns, and lengths of up to several centimeters. The essential feature is, of course, that one dimension is large compared with the others. In one reported case[2], iron whiskers were obtained that were over 80 mm long and 1 to 2 mm in diameter. Whisker cross sections are usually polygonal, with low index planes defining the faces. They occur often as single crystals with the long axis parallel to a prominent crystal direction.

Whiskers do not appear to grow at a uniform rate. Normally, there is a delay, or induction period, then a period of rapid growth, followed by an abrupt cessation of observable growth[3]. Whiskers may be grown under controlled conditions, the most frequently used methods being:

(1) Growth from a solid[4]

(2) Condensation of a supersaturated vapor[5]

(3) Precipitation from solution[6]

(4) Reduction of a metal halide[7].

It is in this latter method of producing whiskers that we have the greatest interest here. However, from the theoretical standpoint, whisker growth by the other three methods has been treated most extensively.

Table 1 presents a partial list of metallic whiskers grown from their halides by hydrogen reduction[8]. These results, arrived at experimentally, represent conditions that favor whisker growth. For example, copper whiskers up to 50 mm long could be grown from cuprous chloride at temperatures between 430 and 850 C. The best results were obtained at 650 C, near the middle of this temperature range. In other regions of the system, the growth of three-dimensional particles or two-dimensional layers may be favored, instead of whiskers. The factors important to one-dimensional whisker growth are as yet largely unknown.

TABLE 1. METALS GROWN FROM THEIR HALIDES
BY HYDROGEN REDUCTION

Metal	Halide	Temperature Range, C	Maximum Length, mm
Cu	CuCl CuBr CuI	430-850	50
Ag	AgCl AgI	700-900	10
Fe	$FeCl_2$ $FeBr_2$	730-760	20
Ni	$NiBr_2$	740	2
Co	$CoBr_2$	650	3
β-Mn	$MnCl_2$	940	0.26
Au	$AuCl_x$	550	2
Pt	$PtCl_x$	800	3
Pd	$PdCl_2$	960	10

The mechanism of whisker formation may be considered from the standpoint of classical nucleation and growth theory.[9] Consider a supersaturated vapor at a high temperature impinging on a crystalline region at a lower temperature. The situation may be represented schematically as shown in Figure 1. This figure shows the surface of a perfect crystal at low temperature with a step in the surface and a "kink" of the type marked A. These kinks play an important part by acting as exchange sites in the positioning of new atoms in order to complete a new layer.

As the temperature is raised, the vibrations of the atoms will become progressively stronger, and some atoms will be able to overcome the energy that binds them to the crystal. This condition is portrayed on the right-hand side of Figure 1, where we see a "rough" surface. Thermal vibrations have produced a high population of states labelled B, C, and D.

Two processes will occur simultaneously: some atoms will leave the crystal, but others will arrive at the crystal from the vapor. An equilibrium state is reached when the rates of these two processes are equal. Growth of the crystal will be the result of three stages: first, a transport of atoms from the vapor to the adsorbed layer; second, the diffusion of adsorbed atoms toward the steps; and third, the diffusion of adsorbed atoms along the edge of the steps toward a kink.
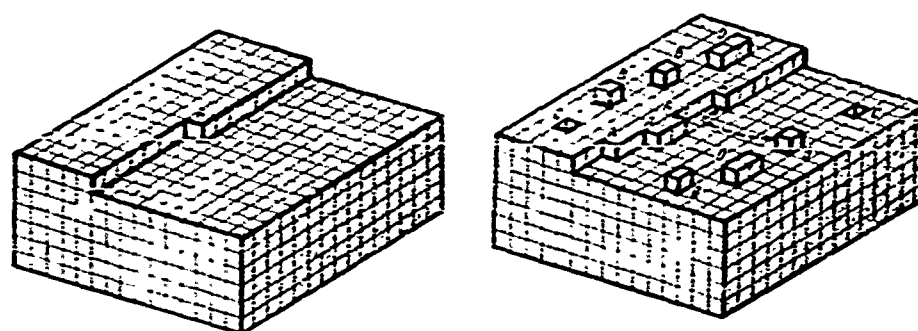
a. At low temperature   b. At higher temperature

FIGURE 1. CRYSTAL SURFACES

Calculations by Burton, Cabrera, and Frank[10] show that atoms diffuse considerable distances before evaporating or sticking. Thus it follows that the rate of growth need not depend on the direct arrival of atoms to any particular place on a crystal surface — such as a kink. Rather, growth can take place by atoms arriving indirectly at the kink by way of surface migration. This point assumes additional significance when considering the growth of whiskers, and will be mentioned later.

Due to the accretion of the atoms, therefore, a straight step will advance, and at a rate proportional to the supersaturation ratio. When the step, or steps, on the crystal surface have travelled to the edge of the crystal, the steps will disappear. Further growth will then be possible only if new steps can be formed.

Gibbs[11] first pointed out that a new layer would have to be nucleated for growth to continue. Thus for a perfect crystal, the factor that limits the rate of growth is the difficulty of starting new layers, which is a nucleation problem. The figure on the left-hand side of Figure 2 represents a two-dimensional nucleus. For a given degree of supersaturation, there is a critical radius of the nucleus, such that for smaller radii, the nuclei will tend to evaporate and for larger radii, the nuclei will grow. The probability that a nucleus of critical size will form is very sensitive to supersaturation.

According to the "classical" theory, two-dimensional nucleation should be impossible at low supersaturations. Moreover, a critical supersaturation of 25 to 40 per cent would be needed for an appreciable rate of formation of nuclei. Yet growth occurs readily under conditions of low supersaturations. In fact, the observed growth behavior is just that which would be expected if nucleation of island monolayers did not occur, but steps were always present on the surface.

F. C. Frank[12] solved the problem of how a surface can remain stepped no matter how far the step advances. He predicted that the growing crystal is not perfect, but contains dislocations similar to that depicted at the right-hand side of Figure 2. Here a screw dislocation meets the surface of the crystal at right angles. As atoms are adsorbed on the surface and diffuse to the step, the step advances on sort of a spiral curve. The surface of the crystal becomes a helicoid (or spiral ramp) and the step can advance indefinitely. Thus, the crystal can grow to any size without the nucleation of new layers.
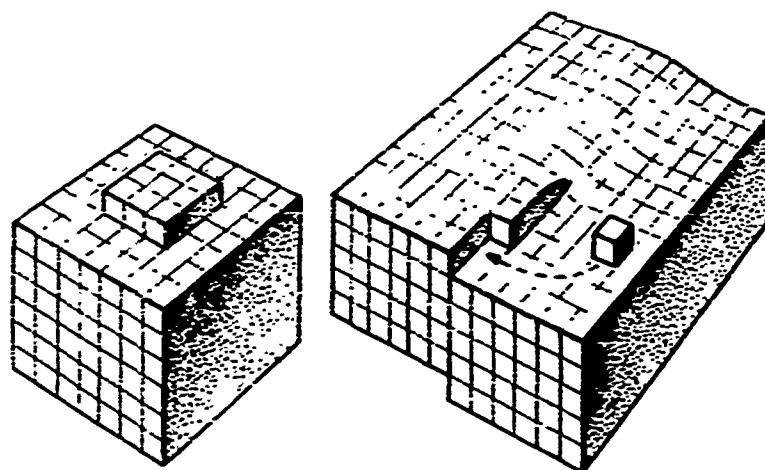
FIGURE 2. CRYSTAL SURFACES WITH A MONOLAYER NUCLEUS
AND A SCREW DISLOCATION NUCLEUS

The theoretical predictions by Frank were brilliantly confirmed by subsequent experimental findings. One such example[13] is shown in Figure 3. We see the surface of a SiC crystal with a growth spiral emanating from a screw dislocation. The step heights are 165 A in this particular case of two-dimensional growth.

The one-dimensional growth that characterizes a whisker is portrayed schematically[14] in Figure 4. The screw dislocation originally present on the surface is seen in the cutaway view, while the tip of the whisker still retains an emergent screw dislocation after growth has occurred.

In some cases a screw dislocation is not readily available at the substrate surface. A mechanism[15] whereby one can be generated is shown in Figure 5. An impurity atom on the surface is engulfed by a growing layer. Under the conditions encountered in this sequence of events, a screw dislocation can be formed.

The success of Frank's screw-dislocation theory of crystal growth prompted several theoretical attempts to explain the growth of metal whiskers. Theories were offered by Peach[16], Frank[17], Eshelby[18], Franks[19], and Amelinckx[20], to name a few. It has been remarked[21] that all these theories require:

(1) A dislocation meeting the surface with a component of its Burgers vector normal to the surface

(2) A dislocation mechanism for generating vacancies at the base of the whiskers

(3) A driving force for this transport mechanism

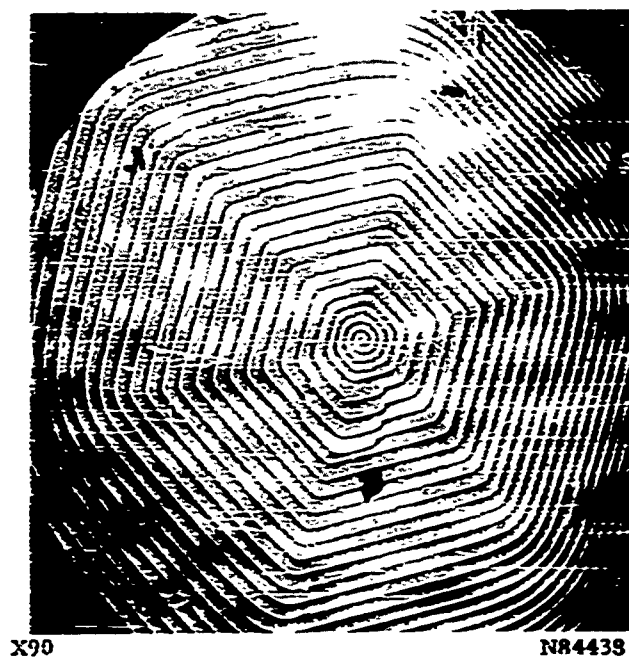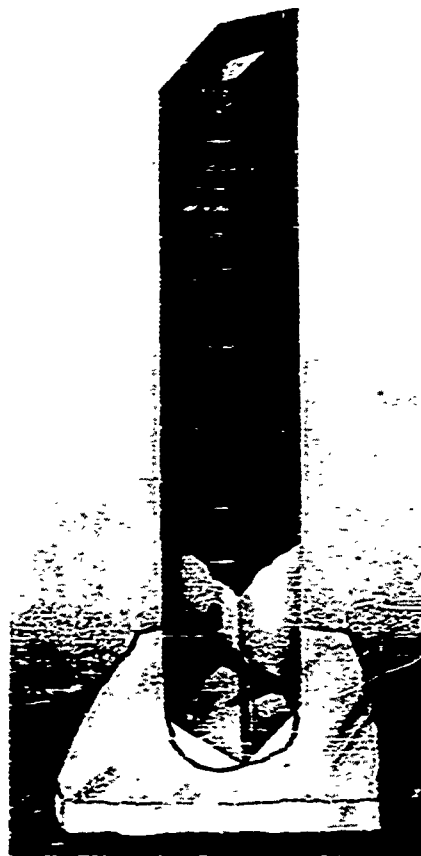(4) A sink for the vacancies that are generated.

X90   N84438

FIGURE 3. HEXAGONAL SPIRAL ON SiC CRYSTAL WITH A STEP
HEIGHT OF 165 A

N84622

FIGURE 4. FORMATION OF A PERFECT CRYSTAL WHISKER
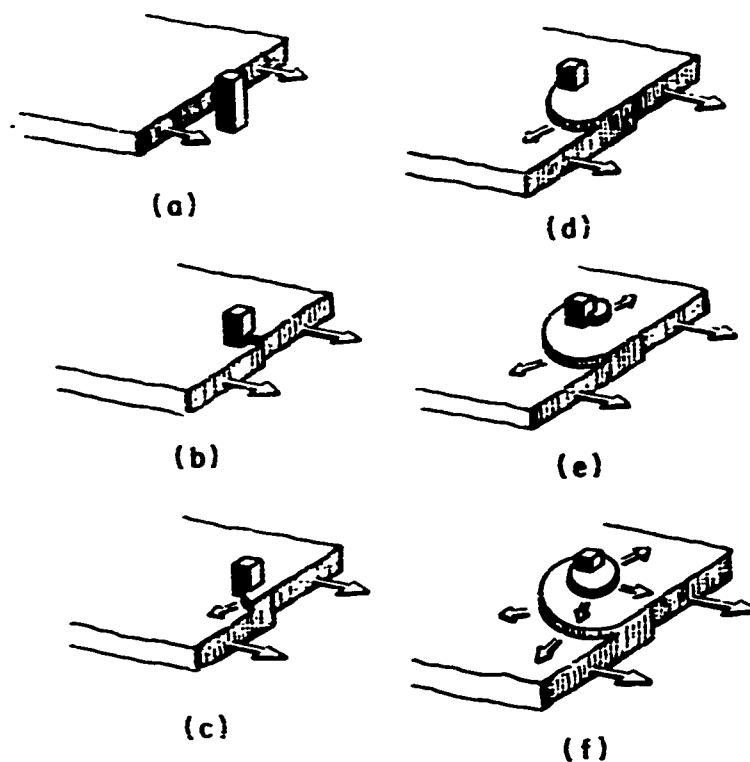ON A SUBSTRATE FROM THE VAPOR

FIGURE .. CAPTURE OF A FOREIGN PARTICLE BY A GROWING CRYSTAL
RESULTING IN FORMATION OF A SCREW DISLOCATION

Other than these four points of similarity, the dislocation theories differ with regard to the details. Figure 7 emphasizes one of the unresolved questions — that is, whether whiskers really grow from their base or their tip. It can be seen that experimental evidence has been obtained for both growth from the base[22] and from the tip[23].

Peach's theory, for example, postulates growth from the tip of the whisker. Figure 6 shows the dislocation mechanism suggested by Peach[16]. The two vertical lines represent screw dislocations emerging at the surface at A and A'. Vacancies diffuse down the dislocation lines, which is equivalent to a movement of atoms up the dislocation lines. The atoms emerging at the surface cause the surface steps to wind in spirals, leading to the formation of whiskers.

Another important dislocation mechanism is one that postulates the growth of whiskers at the base. Examples of these theories are those by Frank[17] or Eshelby[18]. The essential features of a mechanism for growth from the base are described and illustrated in Eshelby's paper. A small hump on the surface becomes oxidized, resulting in a negative surface tension which tends to pull out a whisker. A dislocation source is situated on a plane beneath the hump and gives out dislocation loops which glide to the surface. Each loop adds a single atomic layer to the length of the whisker, causing it to grow from the base.

Other dislocation theories of whisker growth have been advanced. However, they deal mainly with whiskers grown directly from the solid substrate, without participation by other phases. Of more direct interest in this presentation are those whiskers grown by chemical vapor deposition. In this case, we can proceed by analogy with the theory developed for whiskers formed from their vapor. This approach has been adopted by Brenner, and Sears, among others.

Sears[24] studied the growth mechanism of mercury whiskers by condensation of mercury vapor on a glass surface. The actual rate of growth was about 5000 times greater than the calculated growth rate. The calculated growth rate was based on the hypothesis that only mercury atoms striking the advancing whisker tip contribute to axial growth. The discrepancy between the measured and calculated growth rates demonstrates that mercury atoms striking elsewhere are contributing to axial growth.

A calculation of the surface nucleation rate required to account for the observed growth rate also reveals a striking discrepancy when compared with the measured nucleation rate. In terms of the supersaturation ratio, the calculated ratio was about 10^{24} and the measured ratio about 10^3. This result strongly suggests that the axial growth mechanism does not involve nucleation of new layers.

Since the axial growth rate cannot be accounted for by homogeneous two-dimensional nucleation, it is postulated that a permanent growth step is exposed in the advancing step. This is equivalent to the statement that the whisker contains an axial screw dislocation. Since two-dimensional nucleation cannot occur on the whisker faces, and since atomic impingement on the whisker tip is inadequate, Sears postulates another mechanism for rapid axial growth. Mercury atoms impinge on the sides of the whiskers, are adsorbed, and migrate to the advancing end, where they are incorporated into the crystal lattice.
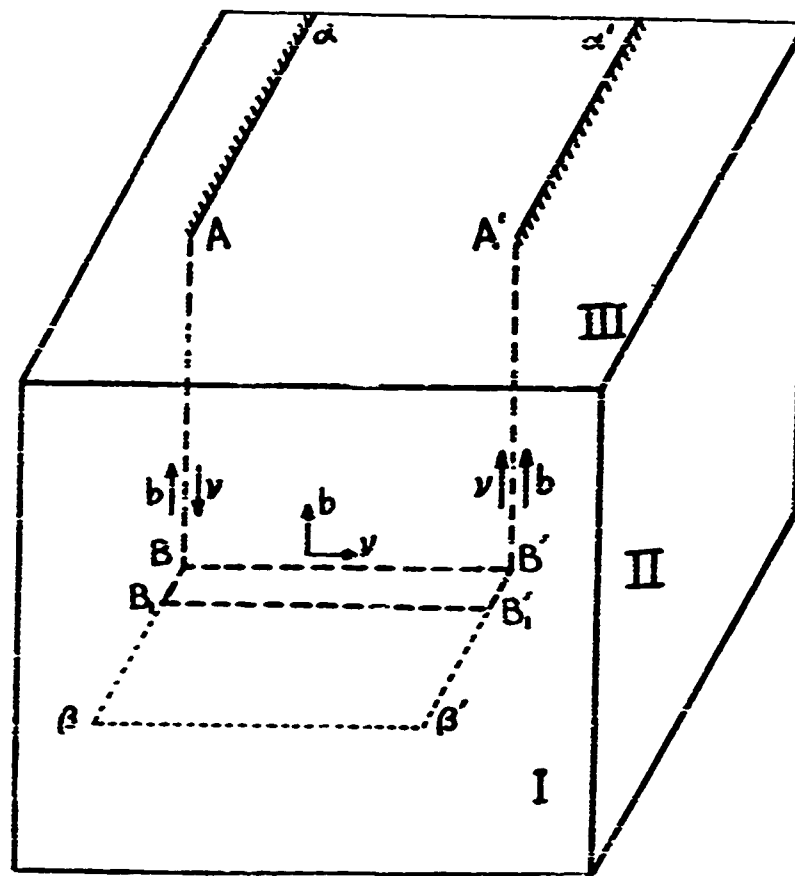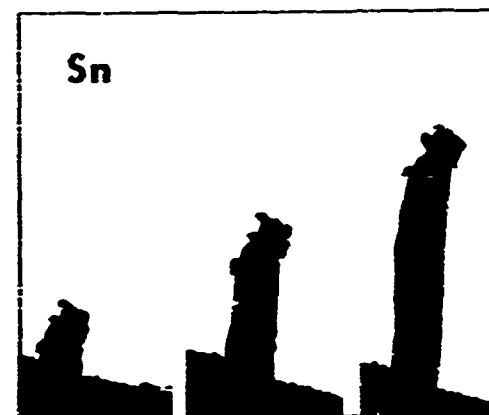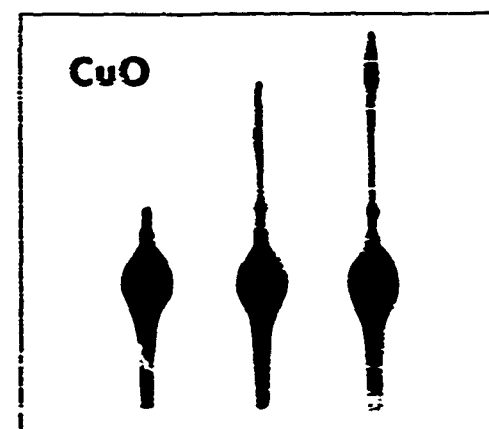
FIGURE 6. WHISKER GROWTH MECHANISM ACCORDING TO PEACH

a. Growth From the Base

b. Growth From the Tip

FIGURE 7. MECHANISM FOR GROWTH OF WHISKERS

The growth rates of whiskers formed by reduction of metal halides should also be explicable by appropriate modification of the above mechanism. However, there is still some question about the details. In particular, two mechanisms were advanced to explain the growth of copper whiskers obtained by the hydrogen reduction of cuprous iodide. Brenner[9] postulated that the reduction of cuprous iodide to copper occurred in the vapor phase, forming a supersaturated copper vapor. Sears[25] felt instead that cuprous iodide acted merely as the carrier species in the vapor phase, and that the reduction of cuprous iodide by hydrogen occurred only at the growth step on the tip of a whisker with an axial screw dislocation.

Brenner's point of view was invalidated by Morelock and Sears[26], who found experimentally that the vapor phase is not highly supersaturated in copper vapor. They concluded that reduction must occur heterogeneously at the tip, which is equivalent to the assumption that reduction occurs at the step of an axial screw dislocation.

In this brief review, no attempt has been made to touch on other interesting aspects of whiskers, for example, their strength properties[27]. Rather, we have tried to summarize the current status of experiment and theory dealing with the nucleation and growth processes of metallic whiskers, and some of the factors controlling these processes.

It is believed that only by a careful quantitative experimental study of the important factors governing whisker growth, in simple systems and under reproducible conditions, can further clarification of this problem be achieved. It has been demonstrated that whiskers can be grown (under empirically developed rules), and that some of these whiskers have attractive properties. It is not unreasonable to expect even greater uses for whiskers that are more perfect, longer, and more stable in ordinary environments. Such properties may be attained more rapidly, the better our scientific understanding of whisker growth.

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THE SCIENCE OF METAL-ORGANIC DECOMPOSITION

by

E. H. Hall and A. Levy

Introduction

In the preceding sections, consideration has been given to questions of chemical vapor deposition as they relate to the deposited material, such as its nature, its form, and characteristics. Let us now consider one of the several available chemical systems from which vapor deposition may be accomplished, namely, metal-organic decomposition.

Metal-Organics as Plating Gases

Several types of metal-organic compounds have been used for the deposition of metals and are summarized below.

Metal-Bearing Compound	Typical Example
(1) Alkyls	$Al(CH_3)_3$
(2) Aryls	$Mg(C_6H_5)_2$
(3) Aralkyls	$Si(C_2H_5)_3(C_6H_5)$
(4) Carbonyls	$Fe(CO)_5$
(5) Acetylacetonates	$Co(CH_3COCHCCCH_3)_2$
(6) Cyclopentadienyls	$Cr(C_5H_5)_2$
(7) Arenes	$Cr(C_6H_6)_2$

It should be pointed out that, for the purpose of this discussion, we are using a broad definition of the term, metal-organic, as have many authors. We include the acetyl-acetonates where the metal is bonded to the organic group through oxygen atoms. Also included are the silanes, although silicon is not a true metal. Because of the diverse types of compounds available, metal-organic decomposition is an extremely versatile tool of chemical vapor deposition. The various compounds available cover a wide range of volatility, stability, toxicity, and ease of preparation. For example. if the toxicity of the carbonyls is a serious objection for a given application, an alkyl might be used. If the metal to be deposited does not form an alkyl, the cyclopentadienyl may be available. Whatever the application, a suitable metal-organic compound can generally be selected.

In addition to deposition of metals, it is often desired to deposit oxides. Work has been reported[1] on the volatile alkoxides of titanium, zirconium, hafnium, and other metals which yield the metal oxide on pyrolysis. A coating of SiO_2 deposited on a semiconductor surface from ethyl-triethoxy silane has been reported.[2] Silicon dioxide and beryllium oxide have also been deposited from ethyl-orthosilicate and beryllium basic acetate, respectively.

In addition to the flexibility of their application, metal-organic compounds offer the advantage that, in general, they can be vaporized and decomposed at relatively low temperatures. Thus, the vaporizer, connecting lines, and deposition surface can be

operated at a lower temperature than when other types of deposition systems are used. This is particularly important in those cases where a metallic coating is to be applied to a substrate which is itself unstable at high temperature. In these cases, metal deposition can be accomplished from some of the carbonyls near ambient temperature.

On the other hand, a severe limitation of the more general use of metal organics is the codeposition of impurities, principally carbon. The common observation has been that, while metal is deposited through a primary reaction, degradation of the organic products through secondary reactions results in contamination of the metal with carbon. Such impurities can be very detrimental as, for example, in the case of the preparation of thin films for semiconductor or superconductor applications where small amounts of impurities can change the electrical properties drastically. It is clear that this problem must be solved in order to make full use of this versatile method. The solution of the problem lies in the proper understanding of the basic mechanism by which the carbon is deposited. By learning the nature of such side reactions, it becomes possible to devise means of preventing them.

Literature

In surveying the recent literature, one finds work divided roughly into two categories. The first is the applied area in which the purpose is to develop a gas plating process. Suitable operating conditions for producing a good deposit are determined empirically. In the second area, other workers have studied the kinetics and mechanism of the decomposition of various metal-organic compounds. Evaluation of any metal deposited was generally not included in the investigation. In a fundamental study, these two approaches must be combined. The kinetics and mechanism of both the primary metal-producing reaction and the secondary reactions of the organic products must be determined and correlated with the observed nature of the metal produced.

In the area of applied work, there is a great amount of literature on deposition from metal alkyls, particularly of aluminum. [3] Considerable art has also been developed in the preparation of metal powders and metal coatings by carbonyl decomposition. Iron, nickel, cobalt, and molybdenum powders and coatings have been prepared in this way for use in the preparation of resistors, porous electrodes, other electrical and electronic applications, and other more general uses. Thin films of cobalt and cobalt-iron alloys have been prepared[4] by deposition from the acetyl-acetonates. Work at Battelle in the applied field has included chromium coating of nuclear fuel particles from chromium dicumene; BeO coating of uranium oxide particles from the acetylacetonate and the basic acetate; molybdenum coating of low-alloy steel for corrosion resistance, iron applied to the inside of small bore stainless steel tubing in a nuclear-reactor application, and nickel coating of porcelain insulators, all from the corresponding carbonyl; platinum from the carbonyl chloride; and copper deposited on glass from the acetylacetonate for electrical conductivity.

Much work on the kinetics and mechanism of the decomposition of metal alkyls has been reported.[5-9] In the great number of cases, the rate-determining step was found to be the breaking of a carbon-metal bond with the formation of a free alkyl radical. The free radicals then react further to yield saturated hydrocarbons as the principal gaseous products. There are cases, however, in which the metal hydride and an olefin,

corresponding to the alkyl group, are produced on pyrolysis. This result is better explained by a molecular rearrangement mechanism than by free-radical formation. Table 1 gives a few cases illustrating both types of reaction. The first four exhibit free-radical formation while the last six are examples of a molecular mechanism in which the

TABLE 1. DECOMPOSITION OF METAL ALKYLS

Compound	Temperature, C	Deposit	Proposed Mechanism[a]	Reference
Germanium tetraethyl	420-450	Ge + ?	--	10
Silicon tetraethyl	560-600	--	FR	11
Silicon tetramethyl	660-720	Si + C	--	12
Tin tetramethyl	430-493	Sn + C	FR + MR	13
Aluminum triethyl	250	--	MR	8
Sodium ethyl	142	NaH	MR	14
Magnesium diethyl	175	MgH_2	MR	15
Beryllium di-t-butyl	210	BeH_2	MR	16
Aluminum tri-i-butyl	150	No metal	MR	17
Aluminum tri-i-butyl	250	Al	MR	17

(a) FR - Free Radical; MR - Molecula Rearrangement

products are metal hydride and an olefin. In some cases, the metal hydride produced can be decomposed at higher temperatures to metal and hydrogen. For example, aluminum tri-isobutyl at 150 C decomposes to di-isobutyl aluminum hydride and isobutylene, while at 250 C, the products are aluminum metal, isobutylene, and hydrogen.[17] It may be seen in Table 1 that those reactions where free radicals have been postulated were carried out at distinctly higher temperatures than those showing molecular rearrangement. It may be that a free-radical mechanism would become important at higher temperatures for the latter group as well. A mode of molecular rearrangement which explains the formation of metal hydride and olefin during pyrolysis is shown below:

Proposed Mechanisms for Metal Alkyl Decomposition

I. "Hydrogen-Resonance-Bridge-Mechanism" of Wiberg and Bauer
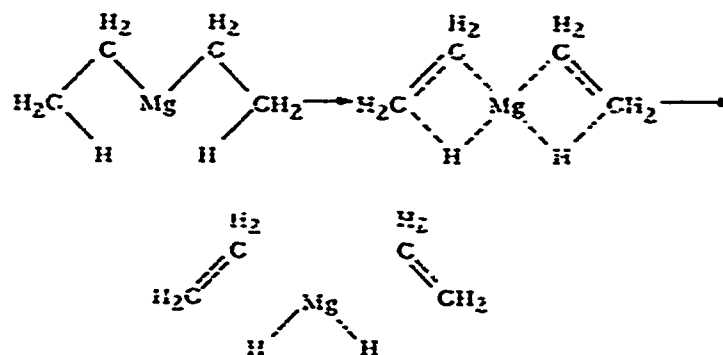
II. Free-Radical Mechanism

$$MR_n = MR_{n-1} + R$$

$$MR_{n-1} = M + (n - 1) R$$
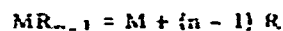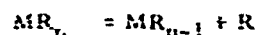
The simple free-radical process is also shown. It will be seen later in the discussion that similar mechanisms are postulated for the decomposition of some organosilanes.

While a considerable amount of work has been done on the kinetics and mechanism of the primary decomposition process, very little has been done to elucidate the secondary processes which lead to carbon codeposition. It is essential that a full understanding of such side reactions be obtained so that means of preventing them can be devised. As an example, in the pyrolysis of mercury dimethyl[18], an oily film of unsaturated hydrocarbons was observed to deposit together with droplets of mercury on the walls of the reaction vessel. When hydrogen was added to the mercury dimethyl before pyrolysis, the rate of reaction was accelerated, and no oily film was deposited with the mercury We may postulate that the hydrogen reacts with the methyl radicals so that they are removed from the reaction more effectively than in the absence of hydrogen. In like manner, there may be many other means of minimizing or eliminating codeposition of carbon or carbon-containing compounds if the mechanism of the secondary processes were accurately known.

An interesting extension of metal alkyl decomposition has been recently reported[19] on the formation of lead telluride films by deposition from mixtures of tetraethyl lead and hydrogen telluride. Films of lead telluride were formed in stoichiometric amounts at a temperature at which the tetraethyl lead is normally stable.

Another recent modification is the use of an electron beam to decompose some metal alkyls.[20] A system is evacuated then back-filled to about 0.5 micron with an organometallic. The substrate to be plated is sprayed with electrons which produce a metal film on the substrate. Presumably, these films are produced with the substrate at a lower temperature than that required for thermal decomposition.

In the work discussed previously, the source materials involved have been more or less unstable compounds which can be decomposed (i.e. reduced) with relative ease to yield the desired deposit. In the case of many organometallic compounds, the decomposition products may be themselves fairly complex organic molecules of differing degrees of stability. Such products must be removed from the deposition site to prevent contamination. A study of the factors affecting the stability of organic molecules thus can be just as useful in providing pertinent fundamental knowledge as is a study of their instability. For the purposes of illustration, a description will be given of work carried out on an Air Force sponsored research program*, in order to indicate some of the techniques which could be employed in an exploration of the kinetics and mechanism of secondary reactions leading to the contamination of deposits with carbon.

Factors That Make for a Stable Organic Molecule

For a molecule to be stable, the rate of decomposition must be low. Expressed in terms of simple reaction kinetics, the rate constant is given by

$$k = Ae^{-\left(\frac{\Delta E}{RT}\right)},$$

where A is the frequency factor and ΔE is the activation energy. In general, for an organic molecule to exhibit good thermal stability, it will possess all or some of the following:

(1) Low k (low A and high ΔE)

(2) Strong C - C bonds

(3) Resonant bonds

(4) Multiple bonds

(5) No hydrogen bonding or strong hydrogen bonding.

With the above criteria in mind, let us consider the results of a study of the decomposition of tetraphenylsilane and its fully hydrogenated derivative, tetracyclohexylsilane.

The kinetic measurements are made by the sealed-vial technique. Decompositions in this program are carried out in the gas phase at pressures between 1/2 and 1 atmosphere. With this procedure, weighed quantities of sample (powder form) are sealed under vacuum and then placed in the furnace for various periods of time. The pyrolized sample is then attached to the vacuum line and the volatile products are transferred, separated, and quantitatively analyzed by standard fractional condensation techniques. These analyses are accomplished with the aid of infrared and mass spectrometric analyses to initially identify the various species. The less volatile components of the reactions, namely, those which cannot be distilled out under vacuum at room temperature, are then analyzed by elevated-temperature gas chromatographic techniques and infrared analysis. Using such procedures, one is able to obtain the rate of formation of the principal products of decomposition, the direct rate of decomposition of the starting material, and also the influence of secondary or competing reactions as a function of the extent of reaction.

Decomposition of Tetraphenylsilane

The primary volatile reaction products of the thermal decomposition of tetraphenylsilane are benzene, smaller amounts of methane and hydrogen, and traces of ethane. These products are formed by a first-order process. Less volatile products are: triphenylsilane and bistriphenylsilylbenzene. In addition, a quantity of polymer is formed which has been shown to contain the silicon still bound to phenyl and other aromatic groups. In Figure 1 is shown a standard first-order plot for the decomposition of tetraphenylsilane at four specific temperatures.

These rate data were then analyzed by a standard Arrhenius-type plot, as shown in Figure 2. One obtains an activation energy of 82.2 kcal/mole. From these combined data, one calculates the rate equation for the decomposition of tetraphenylsilane which is shown in Figure 2.

On the basis of this rate equation and by application of absolute rate theory, one can calculate an entropy of activation for the transition complex and the decomposition reaction. Such a calculation gives an entropy of activation equal to plus 16.2 entropy units. The importance of entropy calculations will be discussed later.

Decomposition of Tetracyclohexylsilane (TCHS)

In the decomposition of tetracyclohexylsilane, the primary product formed is cyclohexene. Much less polymer is produced than in the decomposition of tetraphenyl-silane. Figure 3 shows several plots of the first-order decomposition of TCHS as a function of time and temperature. In Figure 4 are presented two Arrhenius plots for the decomposition based on the rate data obtained from the direct decomposition of TCHS and from the formation of the cyclohexene. As shown here, the activation energies are in fairly good agreement and are indicative of breaking a Si-C bond. The value agrees favorably with the value of the Si-C bond as given by Pauling (57.6 kcal/mole). These data lead to the rate equation given in Figure 4.

Figure 5 shows the influence of substituting a cyclohexyl group for a phenyl group on the silane. In this figure are presented the first-order rate data for the decomposition of (1) tetraphenylsilane, (2) diphenylcyclohexylsilane, (3) triphenylcyclohexylsilane, and (4) tetracyclohexylsilane, all at 476 C. As is quite apparent, the substitution of a cyclohexyl group for a phenyl group markedly decreases stability of the phenylsilane.

In Table 2 are listed kinetic factors for the decomposition of several organosilanes and tetraphenyl germanes. It is of interest to note that the frequency and entropy factors separate the compounds into two distinct groups, suggesting different mechanisms of decomposition. Compounds 1, 2, 3, and 4 have high-frequency factors (i.e., high in the sense that 10^{13} to 10^{14} reciprocal seconds may be called normal according to transition-state theory if the entropy of activation is zero) and correspondingly positive entropy factors. Compounds 5 and 6, on the other hand, have low-frequency factors and correspondingly negative entropy factors. The entropy data suggest that Compounds 1 through 4 go through an initial state to a transition state with no special difficulty (probably just a change from a vibrational degree of freedom in the molecule to a translational degree of freedom in the complex), while Compounds 5 and 6 lose entropy in passing into a transition state by the fact that the activated complex takes on a more complicated structure.
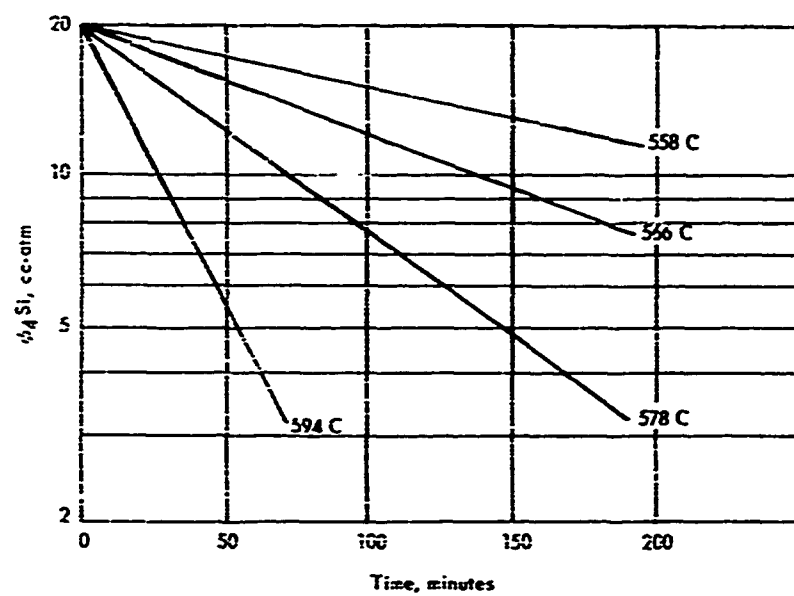
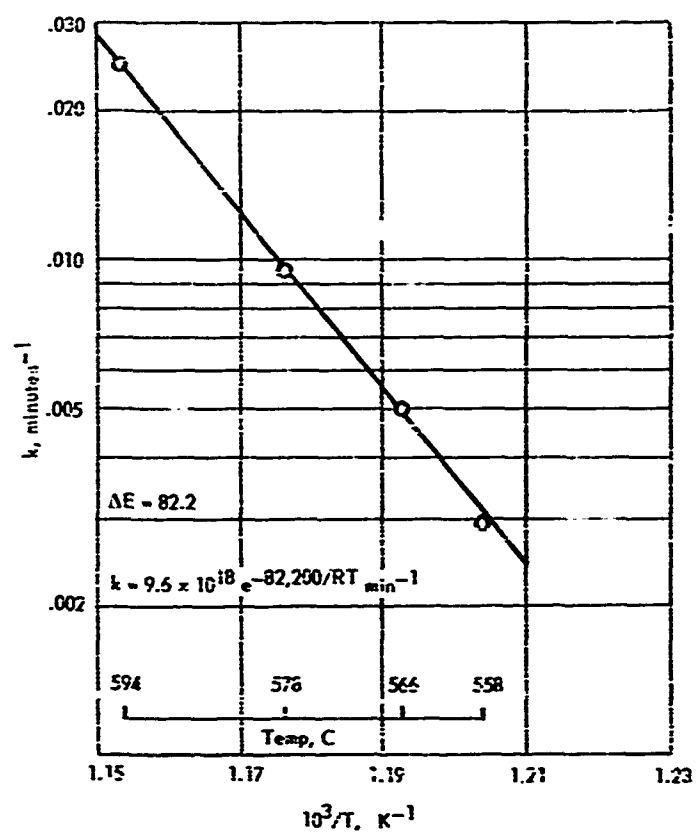FIGURE 1. THE FIRST-ORDER DECOMPOSITION
OF TETRAPHENYLSILANE

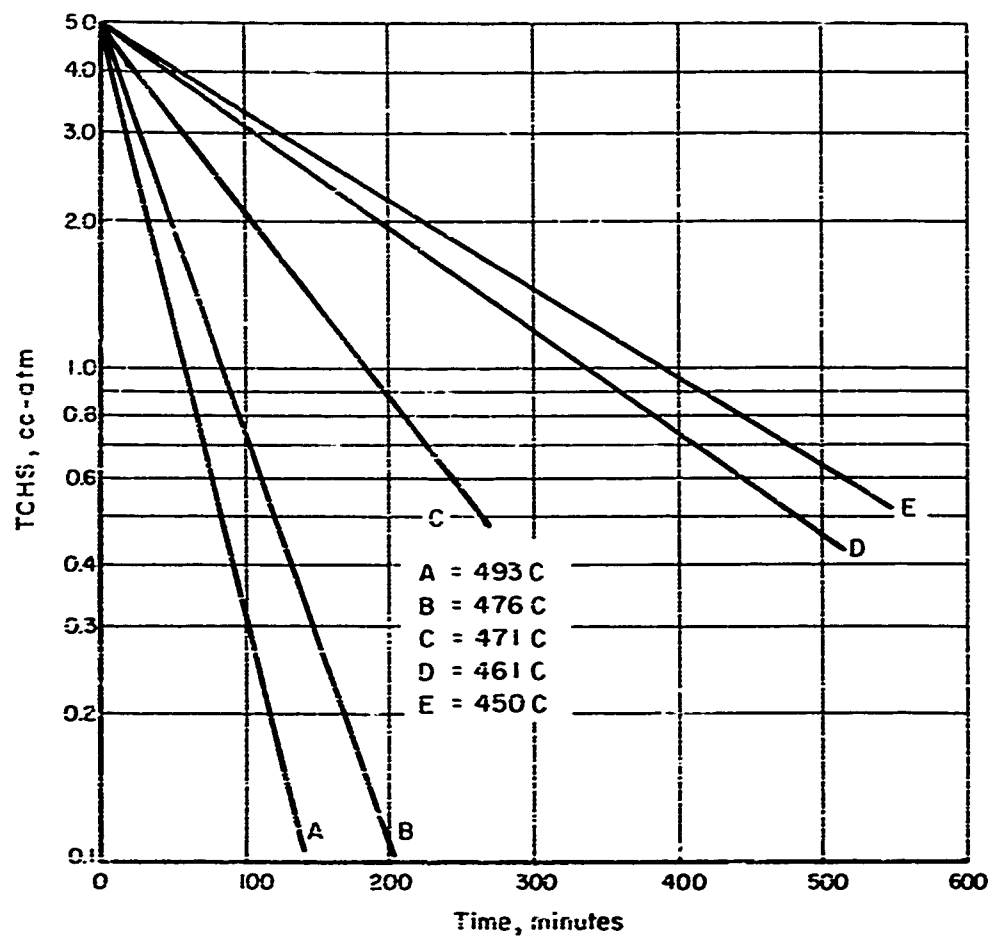FIGURE 2. TEMPERATURE DEPENDENCY FOR THE DECOMPOSITION
OF TETRAPHENYLSILANE

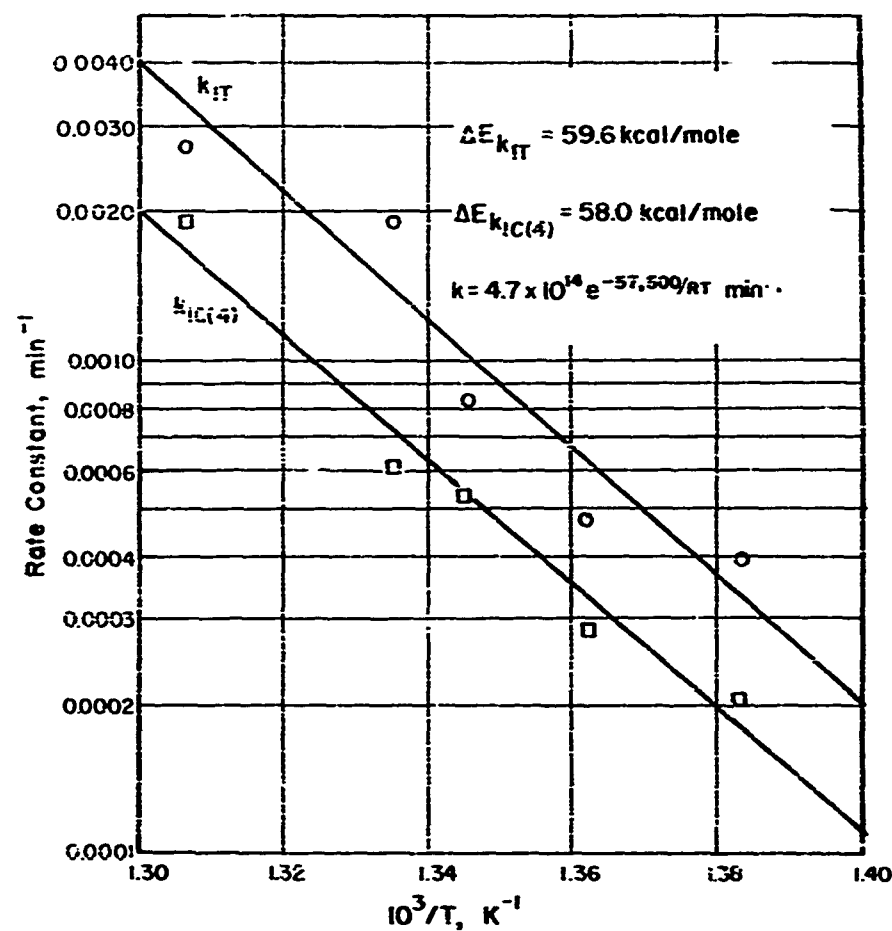FIGURE 3. THE FIRST-ORDER DECOMPOSITION OF TETRACYCLOHEXYLSILANE

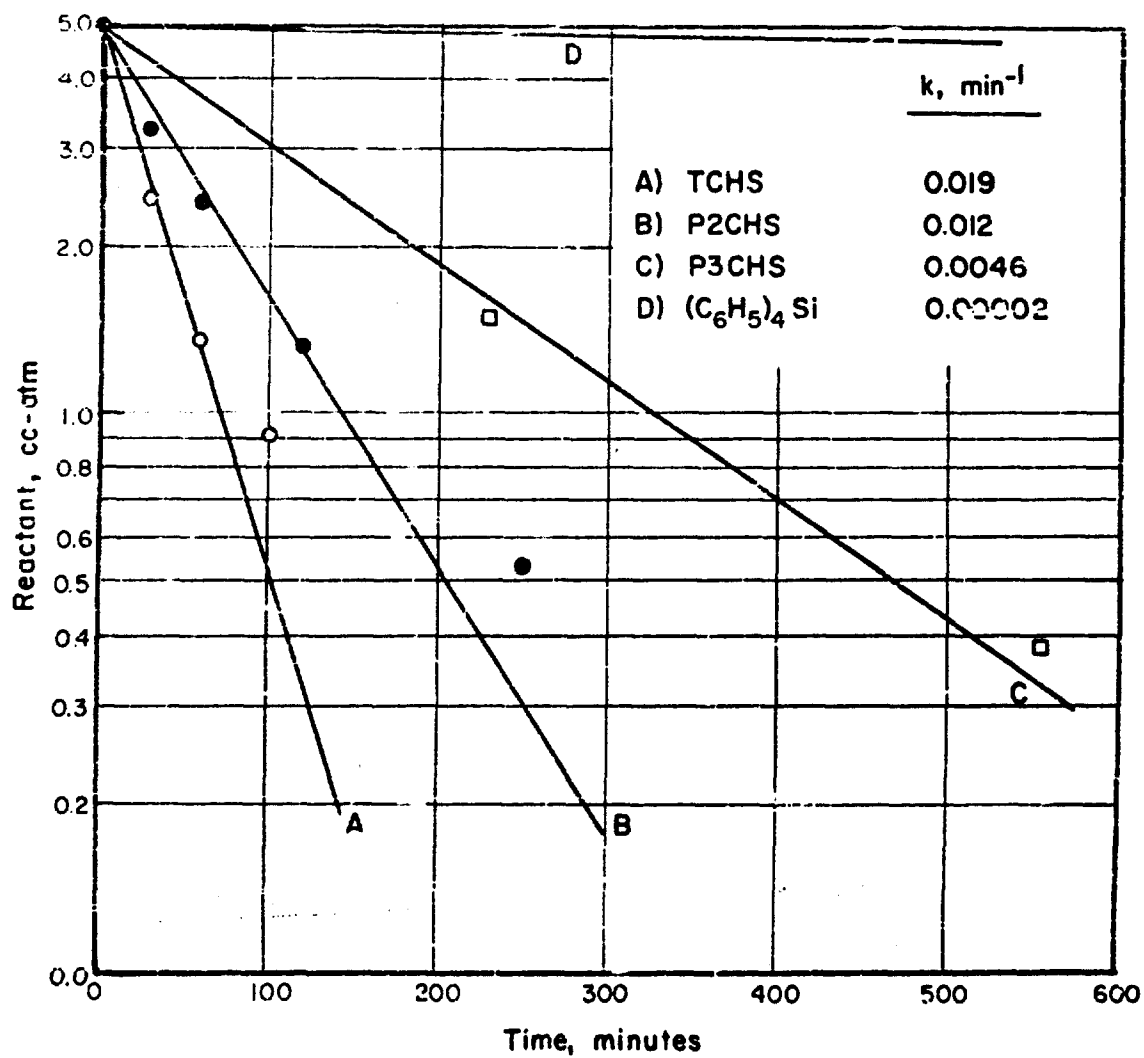FIGURE 4. TEMPERATURE DEPENDENCY FOR THE DECOMPOSITION OF
TETRACYCLOHEXYLSILANE

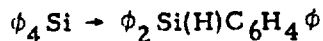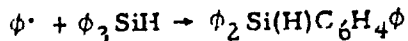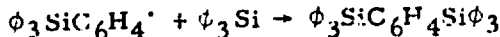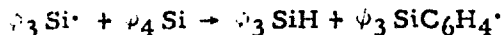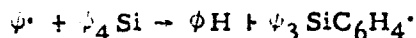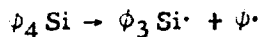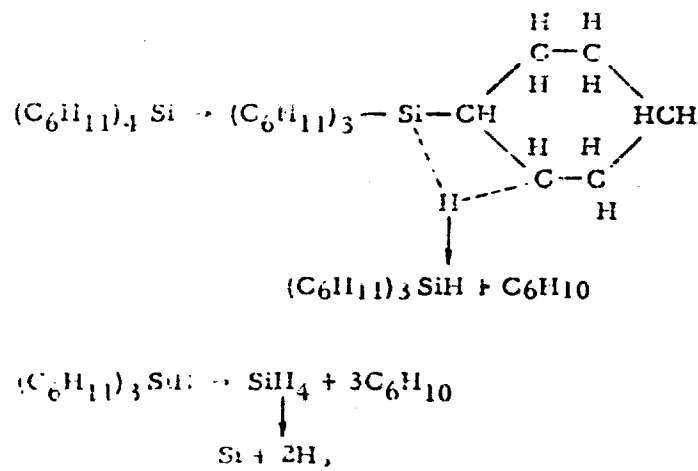FIGURE 5. INFLUENCE OF THE SUBSTITUTION OF CYCLOHEXYL GROUPS FOR
PHENYL GROUPS ON THE DECOMPOSITION OF THE SILANE

TABLE 2. KINETIC FACTORS FOR THE DECOMPOSITION
OF SEVERAL ORGANO-SILANES AND
TETRAPHENYLGERMANE

		Frequency Factor Log A, sec^{-1}	Entropy of Activation (ΔS), e.u.	Activation Energy (E), kcal/mole
I	$Si(CH_3)_4$	15.204	+11.7	78.8
II	$Si(C_2H_5)_4$	16.531	+12.9	50.5
III	$Si(C_3H_7)_4$	15.920	+10.3	46.0
IV	$Si(C_6H_5)_4$	17.204	+16.2	82.2
V	$Si(C_6H_{11})_4$	12.892	-3.2	57.5
VI	$Ge(C_2H_5)_4$	12.505	-5.5	51.0

Stated in still another way, then, these kinetic data suggest that Compounds 1 through 4 decompose by a free-radical process, while Compounds 5 and 6 decompose by an intramolecular process in which the intermediate transition state takes on a four-center-type bond structure. On the basis of these data, therefore, the tetraphenylsilane probably decomposes by a mechanism which follows according to some of the equations given below:

$$\phi_4 Si \rightarrow \phi_3 Si\cdot + \psi\cdot$$

$$\psi\cdot + \phi_4 Si \rightarrow \phi H + \psi_3 SiC_6H_4\cdot$$

$$\phi_3 Si\cdot + \phi_4 Si \rightarrow \phi_3 SiH + \psi_3 SiC_6H_4\cdot$$

$$\phi_3 Si\cdot + \psi_4 Si \rightarrow \psi_3 SiC_6H_4 Si\psi_3 + H\cdot$$

$$\psi_3 SiC_6H_4\cdot + \phi_4 Si \rightarrow \phi_3 SiC_6H_4 - C_6H_4 Si\psi_3 + H\cdot$$

$$\psi_3 SiC_6H_4\cdot + \phi_4 Si \rightarrow \psi_3 SiC_6H_4 Si\psi_3 + \psi\cdot$$

$$\phi_3 SiC_6H_4\cdot + \psi_3 Si \rightarrow \phi_3 SiC_6H_4 Si\phi_3$$

$$\phi\cdot + \phi_3 SiH \rightarrow \phi_2 Si(H)C_6H_4\phi$$

$$\phi_4 Si \rightarrow \phi_2 Si(H)C_6H_4\phi$$

The type of mechanism by which the TCHS is decomposing is as follows:

$$(C_6H_{11})_4 Si \rightarrow (C_6H_{11})_3 - Si - CH \ldots$$

$$(C_6H_{11})_3 SiH + C_6H_{10}$$

$$(C_6H_{11})_3 SiH \rightarrow SiH_4 + 3C_6H_{10}$$

$$Si + 2H_2$$
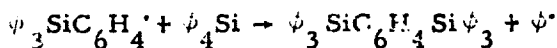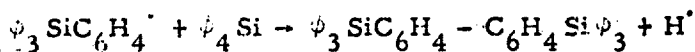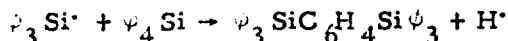
Also shown here is the four-center-type bond structure which exists in the transition state. Although the steps shown appear quite straightforward, and one would assume from this that one would obtain reasonably large quantities of silicon, such is not the case. Free silicon is formed from the decomposition of TCHS, but not to the extent suggested by the above equations. For this reason, therefore, it is quite apparent that there are other reactions which may still tie up some of the silicon.

As we have indicated, the decomposition of tetraphenylsilane does not yield an appreciable amount of free silicon. An infrared trace of the residue which is formed in the decomposition of tetraphenylsilane is shown in Figure 6. The point of principal interest here is the 9.0-micron band and the 14.3-micron band. The 9.0-micron band results from silicon-aromatic bonding in which the broadening of the peaks is due to condensed rings, while the 14.3-micron band represents a silicon-phenyl bond. The top curve as noted here represents the pattern for tetraphenysilane and the bottom curve represents the pattern for the polymer.

A recent Russian[21] study was made of the decomposition of several organo-silicon compounds. This study was primarily directed toward attaining pure silicon. The organosilicon vapor was carried down a reaction tube maintained in a temperature gradient and the deposition of metal was analyzed along the various regions of the tube. Silanes such as tetramethyl, tetraethyl, methyldiethyl, triethylphenyl, allylmethylphenyl, and several other silanes were used. In no instance were the authors able to obtain deposits with less than 25 per cent carbon in the silicon residue. These results are rather consistent with the conclusions obtained from our infrared analysis of the polymeric residue obtained in our own studies. As predicted by structural considerations mentioned earlier, these compounds are all too stable to cleanly yield free silicon.
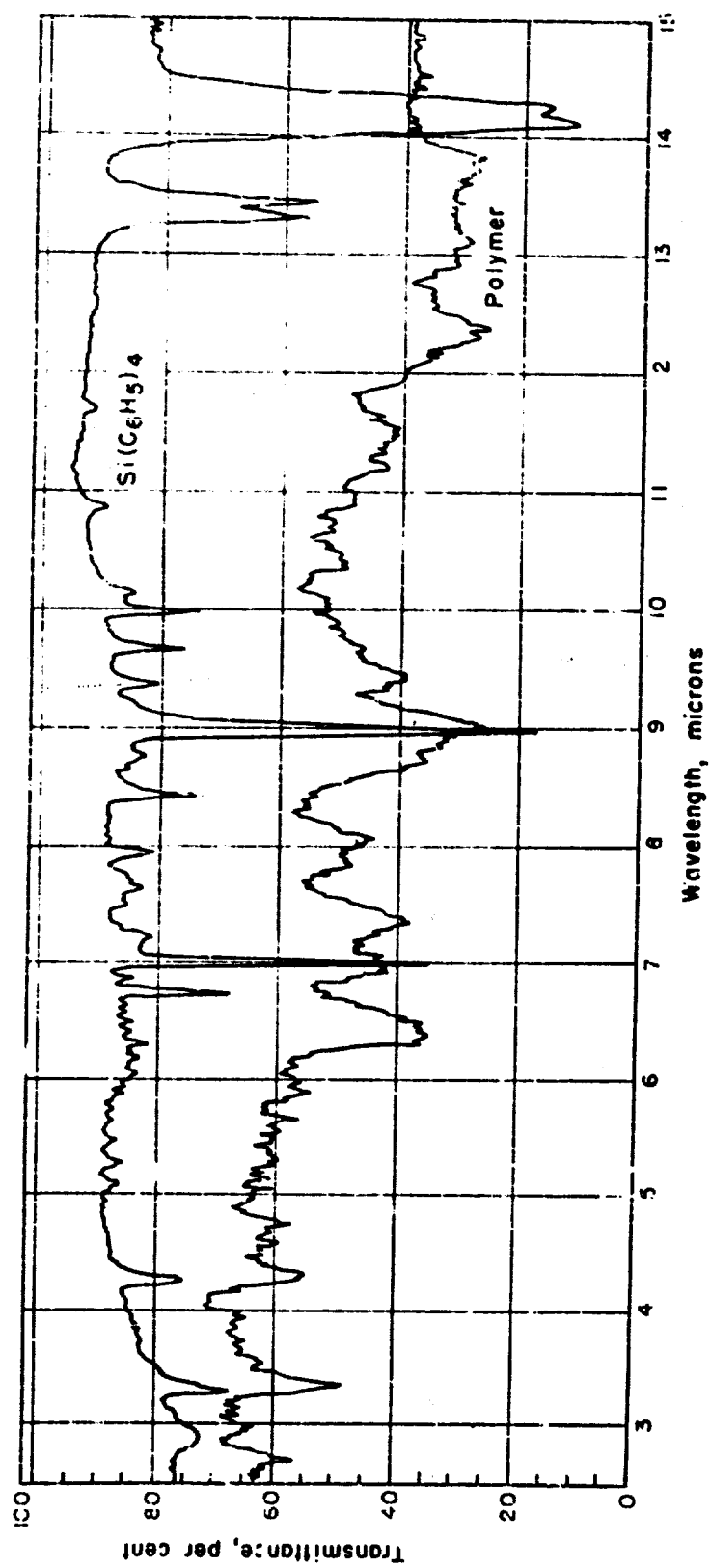
FIGURE 6. INFRARED SPECTRA OF TETRAPHENYLSILANE AND POLYMER

In conclusion, we have seen that metal-organic decomposition is a versatile technique which can supplement and complement the other approaches in the field of chemical vapor deposition. It offers a great deal of flexibility so that deposition systems may be tailored to fit the requirements of a given problem. We have noted that the major obstacle which must be overcome in order to reap the full benefits, is the co-deposition of carbon. In order to solve this problem, it will be necessary to determine the mechanism of the side reactions through which the carbon is deposited. Means may then be devised by which the side reaction may be inhibited. Alternatively, by application of knowledge concerning the effect of structural factors on reaction mechanisms, the structure of the parent compound may be altered so as to provide an organic reaction product which will be less likely to deposit carbon. In addition, the general question of how the metal surface affects the various reactions must be studied. In particular, in the case of the carbonyls, the catalytic effect of freshly deposited metal on the disproportionation of CO must be investigated.

The range of applications of metal-organic decomposition has been extensive — from metallic coating of cloth and paper to coating of tire molds and airplane propellers. But, the future possibilities are even greater. Production of high-purity metals, protective coatings, preparation of thin films of conductors, resistors, and dielectric materials for the fabrication of new electrical and electronic systems — these and many more offer the challenge of the future. We trust that the full potential of metal-organic decomposition will one day be realized.

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FUNDAMENTAL CONSIDERATIONS IN THE CHEMICAL
VAPOR DEPOSITION OF DIFFUSION COATINGS

by

C. A. Krier

Destruction of metals due to physical and chemical interaction with their environments is one of the oldest and, currently, one of the more pressing problems of technology. In the United States alone it has been estimated that metal deterioration currently costs the economy upward of $6 billion annually. Aside from this drain on the economy, it has become important to prevent or at least greatly retard metal deterioration in order to meet the objectives of our rapidly advancing technology and our growing national needs.

Metallurgists, in collaboration with chemists and physicists, have done a commendable job in solving some of these problems through alloy development. However, in other cases, the problems have not been amenable to solution by the alloying approach because (1) the cost of the developed alloy was too high; (2) alloying only lessened the magnitude of the problem without giving an adequate solution; or (3) as is the case with the refractory-metal alloys, when adequate resistance to deterioration is provided by alloying, the resultant materials are unsuitable for the structural applications in which they are needed.

As a consequence, composites, consisting of a structurally satisfactory substrate and a coating, have evolved into a position of considerable technical and commercial prominence. The coating protects the substrate from deteriorating interaction with the environment, and permits it to fulfill its primary structural role.

One of the most important types of coatings in current and anticipated technology is the diffusion coating applied by chemical vapor-deposition techniques. This type of coating has found applicability in both ferrous and nonferrous metallurgy, and at the present time, it has unexcelled popularity among those faced with the most difficult problem of providing reliable protection from oxidation for tungsten-, tantalum-, molybdenum-, and columbium-base alloys.

Aluminizing, boronizing, carburizing, chromizing, nitriding, and siliciding are familiar terms to those of us concerned with protecting metals from their environments by way of diffusion coatings applied by chemical vapor deposition, using either a purely gaseous or a pack process.

It is of interest to examine some of the fundamental factors involved in the formation of these coating systems. Experience gained in this field over the past 15 years indicates that there are many physical, chemical, metallurgical, mechanical, and thermophysical compatibility factors to be considered in attempting to design a good coating system (coating plus substrate). However, for purposes of this brief discussion, it will be assumed that the coating and substrate are compatible with each other and that the properly prepared composite is compatible with its service environment.

Therefore, the major topic under consideration is the bringing together of the substrate and the material to be added to the substrate to form the diffusion coating by chemical vapor deposition.

Consider for the moment the phenomenological approach to analyzing the problem of adding a single coating element, symbolically referred to as C, to the surface of a simple substrate consisting of a single metal symbolized by S. This process involves the following four steps which are shown in Figure 1:
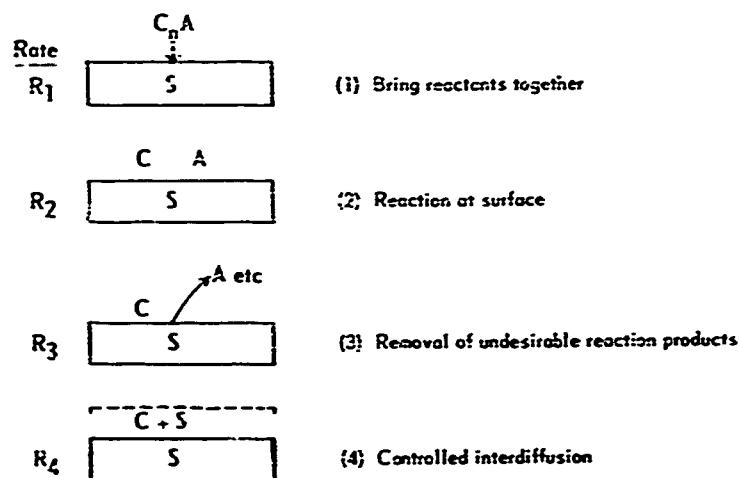

FIGURE 1. STEPS IN THE FORMATION OF DIFFUSION
COATINGS BY CHEMICAL VAPOR DEPOSITION

(1) Bringing of compound containing C, C_nA, together with the substrate S

(2) Reaction at the surface of S to liberate C from C_nA and deposit C on S

(3) Removal of undesirable reaction products from substrate surface

(4) Controlled inter-diffusion of C and S to form the desired coating (case) composition.

The phenomenological analysis reaches its limit at about this stage, and, frequently, considerable experimental effort becomes expended on process investigations which often are carried out on a "go or no-go" basis. This approach should not be slighted by any means, because it sometimes is the only course of action we can follow, due to lack of fundamental information and the urgency for producing hardware. However, the danger inherent in this course of action, and oftentimes realized, is that the effort produces neither the hardware nor the knowledge of how to modify and control the process to produce the hardware.

A closer look at the over-all process raises two fundamental questions:

(1) Along what reaction paths would a proposed chemical system naturally travel, and along what paths could it be made to travel?

(2) How fast can the system travel along the various reaction paths?

The former question revolves around thermodynamics, and the latter involves chemical kinetics.

Thermodynamics is concerned primarily with initial and final states and not particularly with the detailed mechanism whereby reaction occurs; the mechanism enters heavily into the kinetic aspect. Of interest in assessing the thermodynamic feasibility of applying a coating are the volatile compounds available for carrying the coating element to the substrate and the chemical reactions which can deposit the element. Classes of compounds of interest have been hydrides, carbonyls, organometallics, and halides. Types of reactions encountered have been displacement, hydrogen reduction, and thermal decomposition.

Chromizing has been the most thoroughly investigated of the vapor-deposition processes, and it is a convenient example to use to become a little more specific. The three reaction types for the chromizing of iron, using a chloride transfer system, are as follows:

(1) Displacement: $$Fe_{(alloy)} + CrCl_{2(g)} = FeCl_{2(g)} + Cr_{(alloy)}$$

(2) Hydrogen reduction: $$H_{2(g)} + CrCl_{2(g)} = 2HCl_{(g)} + Cr_{(alloy)}$$

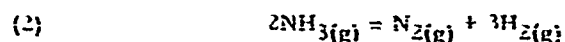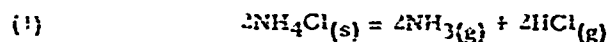(3) Thermal dissociation: $$CrCl_{2(g)} = Cl_{2(g)} + Cr_{(alloy)}$$

Calculation of the free-energy changes for these reactions and the resultant equilibrium constants shows that the displacement and reduction reactions have good thermodynamic feasibility and that the thermal dissociation reaction would not occur to any appreciable extent. (Chromous iodide is less stable, however, and could be used for the thermal dissociation reaction.) Experimentally it has been found that the chromizing of iron can be done by either the displacement or reduction methods, depending on the details of the experiment. It might also be mentioned that similar thermodynamic considerations indicate that the chromizing of nickel and molybdenum is not feasible by the displacement reaction. Where thermodynamic data are available, it can be very profitable to investigate the feasibility of a reaction before proceeding to the laboratory.

The formation of diffusion coatings by chemical vapor deposition is done using flowing gaseous or static pack processes. An examination of a pack process is rather interesting both from the thermodynamic and kinetic viewpoints.

A simple pack process involves imbedding the pieces of metal to be coated in a powder mixture consisting of the metal to be plated, an "energizer", and usually an inert material to prevent sintering. The powder mixture in a chromizing pack might consist of Cr and NH_4Cl, with Al_2O_3 as the inert filler. After the pack is assembled in a container called a retort (a simple box which may or may not be sealed), the assembly is heated in a furnace to a given temperature, held at temperature for a time, and then cooled.

The action which occurs in a pack, using the chromizing of iron again as an example, can be viewed as consisting of several steps, the exact chemistry of which has not been documented in complete detail.

$$(1) \qquad 2NH_4Cl_{(s)} = 2NH_{3(g)} + 2HCl_{(g)}$$

$$(2) \qquad 2NH_{3(g)} = N_{2(g)} + 3H_{2(g)}$$

$$(3) \qquad Cr_{(Alloy\ 2)} + 2HCl_{(g)} = H_{2(g)} + CrCl_{2(g)}$$

$$(4) \qquad CrCl_{2(g)} + Fe_{(Alloy\ 1)} = FeCl_{2(g)} + Cr_{(Alloy\ 1)}$$

$$(5) \qquad FeCl_{2(g)} + Cr_{(Alloy\ 2)} = Fe_{(Alloy\ 2)} + CrCl_{2(g)}$$

$$2NH_4Cl_{(s)} + Cr_{(Alloy\ 2)} = N_{2(g)} + 4H_{2(g)} + CrCl_{2(g)}$$

$$Cr_{(Alloy\ 2)} + Fe_{(Alloy\ 1)} = Cr_{(Alloy\ 1)} + Fe_{(Alloy\ 2)}$$
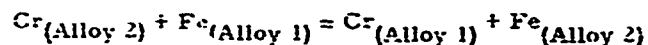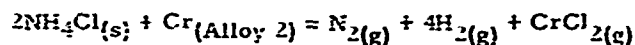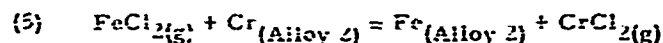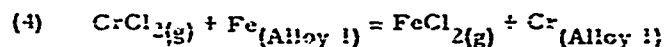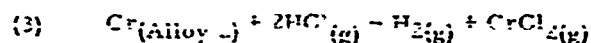
The last two equations, which are obtained by adding the preceding five equations, show that the over-all chemistry is that of a concentration cell in which transfer can be made in both directions; and the role of the salt is to "energize" the pack and provide a gaseous transport path. In effect, a double displacement reaction is carried out, and the driving force is derived from the difference in activities of chromium and iron at different locations. Initially, the activities of chromium and iron in the powder are unity and zero, respectively. If the system behaved ideally, the reaction would be expected to stop when the concentration of chromium and iron in the pack metal powder (Alloy 2) and at the coating surface (Alloy 1) reached 50 atomic per cent. Experimentally, chromium concentrations at the surface of chromized steel have been found to be between 35 and 50 per cent.

Now let us turn our attention to the kinetics of the pack chromizing of iron to gain an insight into rate factors which can enter into the formation of diffusion coatings by way of chemical vapor deposition. The general rule is that the rate of the slowest step in the sequential process will control the rate of the process.

Review of the above reactions for pack chromizing shows that the initial step is the energizing of the pack (Reactions 1 and 3). If the vapor pressure of the energizer were extremely low at the experimental temperature or if the thermodynamic stability were very high relative to that of the plating compound, the over-all reaction might not even get started, or might at best proceed at an impractically low rate due to a low concentration of the plating compound.

Although the thermodynamic driving force of the plating reaction (Reaction 4) at the substrate surface might be high, this is no guarantee that the rate of deposition will be practical. In addition, the volatility of the reaction by-products (FeCl$_2$, Reaction 4, for the example under consideration) must be sufficiently high that removal can be easily accomplished, or they could form a barrier to continued plating action. Removal of the by-products can be highly important from another standpoint also, namely that of contamination of the coating with subsequent poor performance in service.

Transport of gases to and from the substrate involves movement by way of gaseous diffusion through the pack. Should the pack undergo appreciable sintering or be compacted too tightly, chemical-reaction rates could be impaired.

If the supply of coating material is adequately maintained at the surface of the substrate, then the rate of growth of the coating will be determined by the rate of inter-diffusion of the coating and substrate elements. An exact estimate of the rate of growth of a coating from diffusion coefficients is difficult because, often, more than one phase is present in the coating, and in addition, the small quantities of impurities which may be present in commercial metals can have a pronounced effect on diffusion rates.

From diffusion theory, coating thickness and time at a given temperature can be related by the equation

$$X^2 = 4 \, ADt,$$

where X is coating thickness, A is a constant involving the concentration of the diffusion element at the surface, D is the diffusion coefficient (assumed to be independent of concentration), and t is time. With the known relationship between diffusion coefficient and temperature, $D = D^* e^{-B/T}$, the coating thickness can be related simultaneously to both time and temperature:

$$\log \frac{X^2}{t} = C - \frac{B}{T} \quad .$$

This relationship is quite general in its application, but the constants are unique for each diffusion system, and, therefore, separate sets of constants are required for each phase field in the diffusion zone.

Some of these aspects of diffusion can be illustrated with results obtained in the chromizing of steel. According to diffusion theory, the rate of transfer of a diffusing element across unit area of a diffusion interface is related to the concentration gradient by

$$J = -D \left(\frac{\partial C}{\partial X} \right) \quad .$$

At normal chromizing temperatures, steel is in the γ or austenitic phase which is face-centered cubic. However, when above about 13 per cent chromium is contained in the steel, the structure changes to the α or ferritic phase which is body-centered cubic. It is known that the diffusion coefficient of chromium in the α-phase is about 50 times larger than that in the γ-phase. Therefore, at the interface at 13 per cent chromium, because instantaneously as much chromium must diffuse into this interface as diffuses out,

$$D_\gamma \left(\frac{\partial C}{\partial X} \right)_\gamma = D_\alpha \left(\frac{\partial C}{\partial X} \right)_\alpha \quad .$$

But $D_\alpha > D_\gamma$, and thus $\left(\frac{\partial C}{\partial X} \right)_\alpha < \left(\frac{\partial C}{\partial X} \right)_\gamma$. In other words, the chromium gradient

will be expected to be shallow in the α-phase relative to that in the γ-phase. Figure 2 shows that this has been confirmed experimentally.
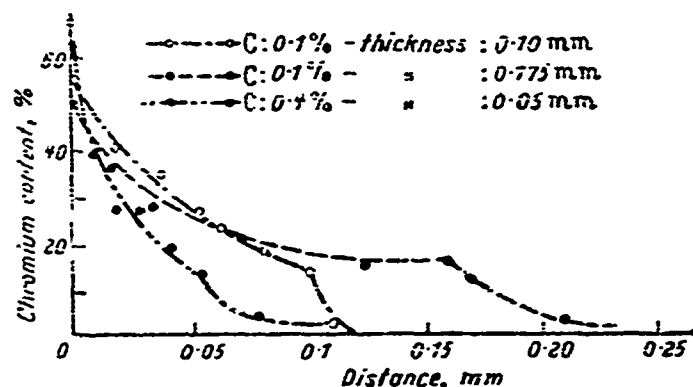
FIGURE 2. CHROMIUM UPTAKE AS A FUNCTION OF DISTANCE
FROM THE SURFACE FOR CHROMIZED STEELS

(After P. Galmiche, as given in Reference 4).

The fact should not be overlooked that the rate-controlling mechanism may change during the formation of a coating due to the continuously changing chemistry of the surface layers and the length of the diffusion path. Also, it should be noted that the performance of the coating is determined in large part by the chemical concentrations at and near the surface, and these can be changed by a change in the rate-controlling mechanism. For example, if the rate of plating is the slowest step of the process, a lower surface concentration and a shallower gradient of the coated element would be expected than if diffusion were the rate-controlling step.

There are many additional factors involved in the formation and performance of chemically vapor-deposited diffusion coatings than the thermodynamic and kinetic aspects briefly exemplified for the relatively simple case of chromizing iron. Personnel at Battelle have been and continue to be heavily involved in research on the many problems associated with the protection of steels, superalloys, and the refractory metals by the use of diffusion coatings applied by chemical vapor-deposition techniques.

One of the processes which has received much attention in recent years is the siliconizing of molybdenum to form a coating of $MoSi_2$ which is very resistant to high-temperature oxidation.[10] Today the $MoSi_2$-base coating is very much in the limelight, and it has achieved commercial stature. However, considerable effort is currently being expended to bring the coating system to a better degree of perfection. Variables investigated in recent studies[11] include purity, particle size, and mixing of pack constituents; surface contamination and preparation of the substrate; and time, temperature, and retort composition used for processing.

In the development of diffusion coatings for tantalum-base alloys[12], two major subproblems have been encountered. These are: (1) selection of coating compositions having the proper compatibility relationships with the substrate and the intended service environments, and (2) formation of the desired coatings to produce systems having high reliability. Neither of these problems is simple, and frequently the empirical approach to solution has been the only route available due to several factors.

The multiplicity of alloying elements involved in tantalum- and columbium-base alloys and in superalloys and the frequent desire for the chemical vapor deposition of several additional elements make the problems quite complex from the standpoint of carrying out rigid analytical studies. At this stage of relative infancy in the science of chemical vapor deposition of diffusion coatings, the chemistry of even the simplest systems is not completely understood.

Performance of a coating system in general cannot be divorced from preparation, and preparation is a good deal more complex than a "go or no-go" operational procedure would suggest. Much fundamental investigation needs to be done to move the general preparation of chemically vapor-deposited diffusion coatings from its present status of predominantly art to one of science.

In the field of thermodynamics, more reliable and more complete data are needed to predict reaction feasibility and useful conversions. Better methods for predicting feasible reaction paths in multicomponent systems would be most useful.

Identification of rate-controlling steps and determination of how the rates vary with chemical concentration, temperature, pressure, and possible catalytic effects are needed. Diffusion in complex alloys and the effects of minor additions and temperature changes should be studied.

A sound collection of thermodynamic and kinetic information would allow us to ascertain the causes (of which there could be many) of apparent failure in systems which did not "go", and properly control and perfect those systems which do go.

Multicycle deposition and codeposition are areas of much needed research, and, I believe, of much untapped fertility. Figure 3 shows an example of benefit derived from multicycle deposition; it also shows that the order in which the depositions are
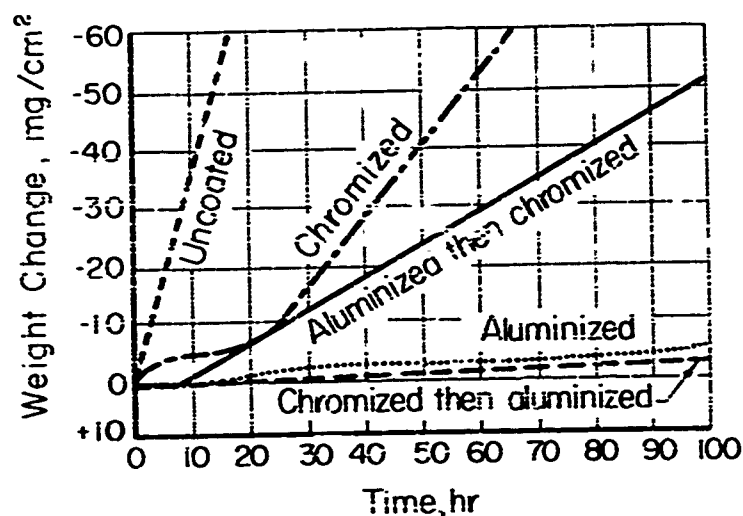
FIGURE 3. OXIDATION RESISTANCE OF COATED HASTELLOY ALLOY B AT 2000 F

(After J. R. Schley, Reference 7).

carried out can have a profound effect on the nature of the coating produced. Valuable input to this field of investigation should come from a comprehensive collection of thermodynamic and kinetic information. Also, liberal use should be made of such research tools as the electron-probe microanalyzer, which already has yielded much useful information. This is not an inexpensive tool to use, but it is an indispensible tool for genuine scientific progress to be made in the areas of multicycle deposition and codeposition.

The role of substrate geometry in the formation and performance of diffusion coatings requires quantitative definition, particularly for relatively brittle coatings. Figure 4 shows a type of coating imperfection resulting from unfavorable substrate geometry, namely irregular surface finish and too small a radius on an edge. Figure 5 shows the structure of this same coating system on a flat surface. Hairline cracks exist, but the large V-type defects shown in Figure 4 are absent. This coating system is inherently excellent. However, if it is not properly prepared it can be devastatingly unreliable. A very major factor determining reliability is known to be the substrate geometry, but a quantitative relationship between geometry and performance is not yet known.

A large columnar grain structure generally is characteristic of vapor-deposited diffusion coatings. Metallurgically this type of structure is rather weak. Studies to determine if and how the grain structure could be altered and controlled in diffusion-coating systems are very much in order. Input to this area from general studies of nucleation and growth mechanisms in chemical vapor deposition should be of considerable value.

We have already indicated that reliability is a major problem in currently promising vapor-deposited coating systems. Detailed and methodic investigation is urgently needed to identify the fundamental causes of premature localized failures. The roles of dislocations, vacant lattice sites, interstitial impurity atoms, adsorbed gases, stresses, and microscopic geometry at the substrate surface in the over-all problem of attaining high reliability are, at the present time, only subjects of speculation.

In summary, we believe that chemically vapor-deposited diffusion coatings have a bright future. This area of technology is based predominantly on art rather than science at the present time. There are many problems requiring solution. If the science is developed, we believe these problems will be solved, and the technical and commercial potential of chemically vapor-deposited diffusion coatings will be realized.

100X   N71766

FIGURE 4.   V-TYPE DEFECTS IN A BRITTLE COATING
            RESULTING FROM IRREGULAR SURFACE
            FINISH AND TOO SMALL A RADIUS ON THE
            EDGE OF THE SUBSTRATE
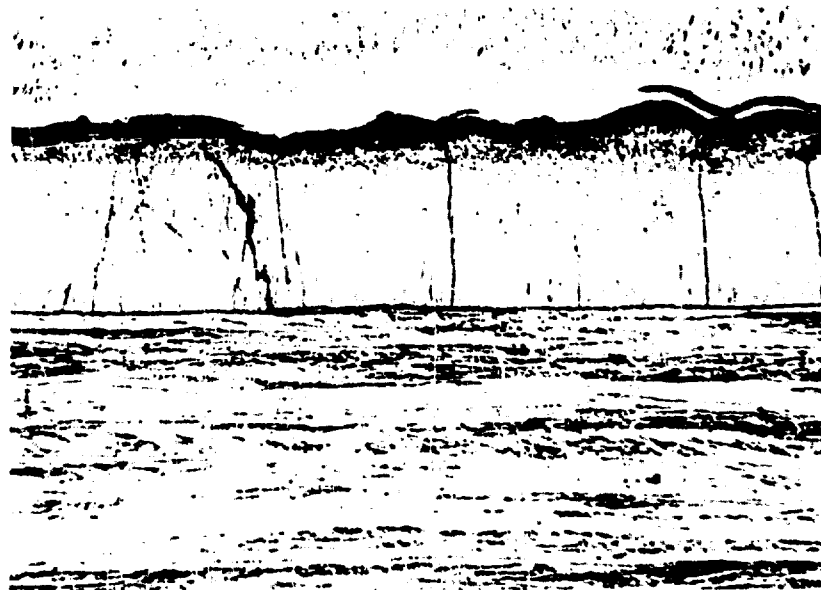
250X   N74748

FIGURE 5.   STRUCTURE OF COATING ON A FLAT SURFACE
            OF THE SYSTEM SHOWN IN FIGURE 4

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VAPOR-PHASE-TRANSFER PROCESSES DURING CHEMICAL VAPOR DEPOSITION

by

J. H. Oxley

Introduction

The first published work demonstrating the significance of diffusion processes during chemical vapor deposition was a result of investigations carried out at Sylvania Electric Products.[1] In this study it was demonstrated that the rate-determining step in the de Boer - Van Arkel process for iodide zirconium was the diffusional transport of gaseous reactants. This was a very important discovery, and is the basis for most of the mathematical treatments which follow. Later analyses of chemical vapor-deposition processes, particularly by German workers[2], suggested three mechanisms which occur in three different pressure ranges. These are listed below:

(1) Reaction rate is controlling, and diffusion resistances are negligible at pressures less than 1 mm Hg.

(2) Simple diffusion is controlling transfer rates at pressure levels between 10 and 760 mm Hg.

(3) Convective transport is the controlling factor at pressures greater than 1 atm.

Fortunately, from an applications standpoint, the situation is not so restrictive as just outlined, and considerable overlap of these mechanisms can be brought about by processing variables. This variability can provide improved control over the process, but makes data analysis more complicated and can result in disappointment and failure in attempting to apply the laboratory studies to a commercial venture.

In order to summarize the state of the art, the pertinent technology will first be very briefly reviewed from the standpoint of surface deposition controlled by chemical reactions. Then emphasis will be placed on surface deposition when controlled by gas-phase diffusion. No careful analysis of the problem of natural convection during deposition has yet been performed, so this item will not be included in this review.

Surface Deposition – Gas Kinetics Controlling

An example of a vapor-deposition process which is controlled by simple reaction kinetics can be found in some recent work carried out for the Atomic Energy Commission.[3] The equipment used in this study of kinetics is shown in Figure 1. Hydrocarbon vapors were passed up through a shallow fluidized bed of fuel particles having good heat- and mass-transfer characteristics. The rate of carbon deposition was then studied as a function of the processing variables.

By the use of the relationship shown in Equation (1), the rate of carbon deposition (W) was correlated with the surface area of the particles (S), the temperature of the bed (T), and the partial pressure of the reactant hydrocarbon (P_i):
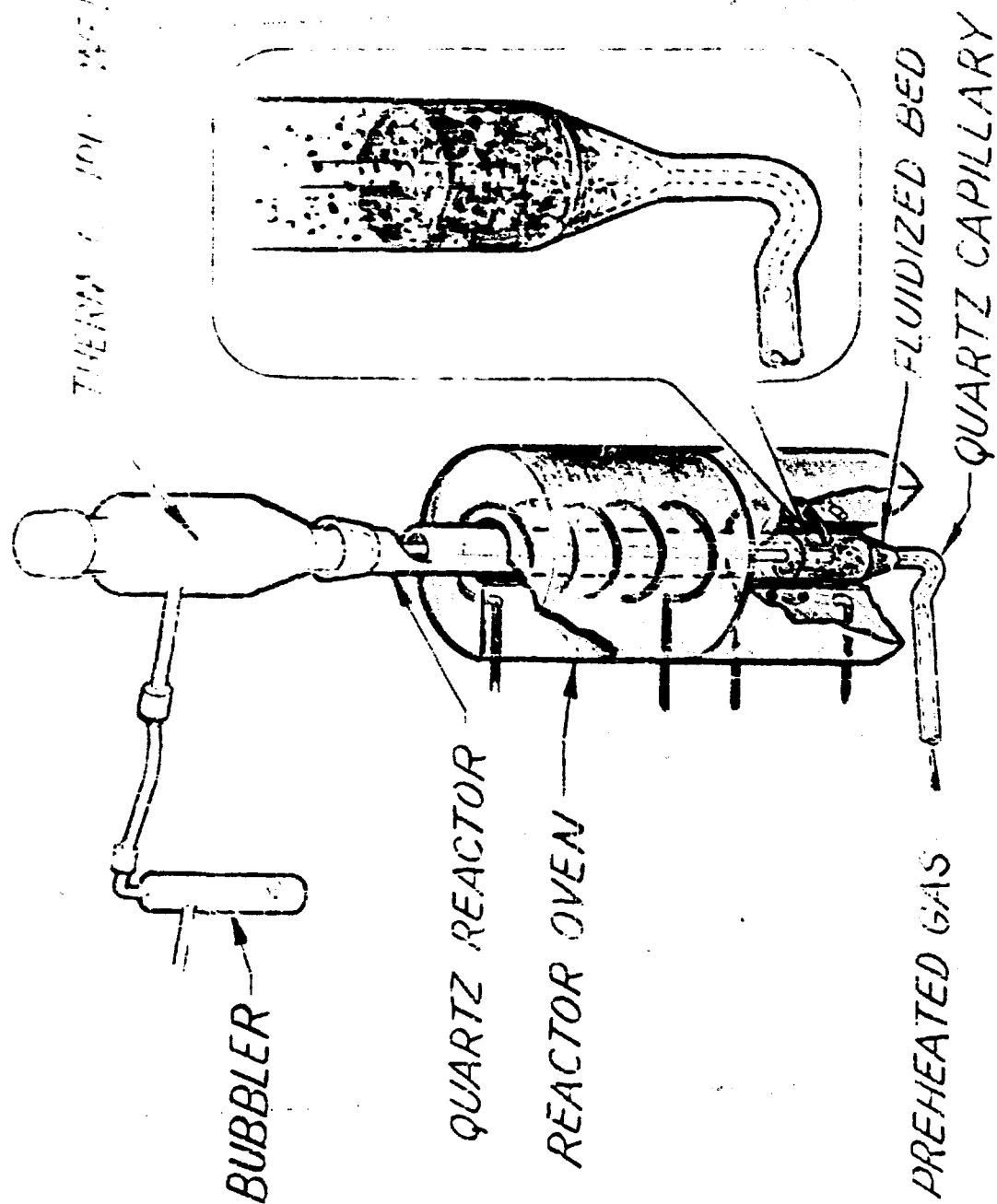
FIGURE 1 APPARATUS FOR COATING POWDERS WITH CARBON

$$W = \frac{k_o \, P_i^n \, S^{a+1} \, e^{-E_i/RT}}{T} \quad . \tag{1}$$

The results of this study showed that the reaction orders and activation energies were the same as for simple gas-phase pyrolysis, as shown below:

Constants	Methane	Acetylene
Activation energy, E_i	90.4	51.0
Partial-pressure exponent, n	1.30	1.45
Surface-area exponent, a+1	1.39	0.92
Specific rate constant, k_o	3.68×10^{14}	2.80×10^{10}

Thus, the carbon-deposition rate on the surface of the bed particles was controlled by the rate of pyrolysis of the hydrocarbons in the temperature ranges studied, i.e., 700 to 1100 C. At sufficiently high temperatures, perhaps 1500 C, the kinetics of the reaction is so rapid that the controlling mechanism will probably shift to one of diffusional control. Under these conditions, there is ample carbon available for deposition, but the diffusional transport of hydrocarbon to the surface of the particles is low compared with the pyrolysis rate. Diffusion would therefore become the rate-limiting step.

Surface Deposition — Gas Diffusion Controlling

As shown in Equation (2), under steady-state conditions, gas-diffusion rates can be correlated with an equation relating the rate of deposition to the molecular weight of the depositing species (M_w), a mass-transfer coefficient (k), the area to or through which diffusion occurs (A), and a diffusion potential (Δy) related to the concentration gradient in the system[4]:

$$W = M_w k A \, \Delta y \quad . \tag{2}$$

In some cases, particularly in the absence of either natural or forced convection, this equation can be an exact solution of Fick's law, and the various factors can be determined theoretically. In other cases, generally for situations of complicated geometry or flow pattern, the various factors must be determined experimentally and the evaluation may, therefore, become semiempirical. Methods of evaluating the last three factors in Equation (3), i.e., the coefficient, the area, and the driving potential, will now be reviewed for various practical processing situations.

Evaluation of Mass-Transfer Coefficient

The relationship shown in Equation (3) is used in the evaluation of the mass-transfer coefficient (k), for the simplest situation involving pure diffusion, i.e., no convection, across a length (Z) of constant cross section. The mass-transfer coefficient in such a situation can be calculated from the diffusion coefficient (D_v), pressure (P), gas constant (R), and temperature (T)[5]:

$$k = D_v P/ZRT \quad . \tag{3}$$

This equation has been extensively used by German investigators to correlate the vapor transport of silicon by its halides.[2]

The next equation shows that, for ideal flow across a cylinder of specified diameter, a relationship similar to one originally developed by British workers for heat transfer can be employed[6]:

$$k = \frac{D_v P}{\pi d R T} \quad . \tag{4}$$

Here the length term (Z) found in the previous equation is simply replaced by the product of π and the cylinder diameter (d).

An investigation on the real flow of titanium tetraiodide across a heated cylinder was carried out in the apparatus shown in Figure 2.[7] The reactant vapor entered the unit from the left, and the coefficients for the average rate of titanium deposition were correlated as a function of the processing variables. The appropriate formula which accounts for the effect of the Reynolds (N_{Re}) and Schmidt (N_{Sc}) Numbers on the transfer rates is shown in Equation (5):

$$k = \frac{D_v P}{d R T} \left(N_{Sc} \right)^{1/3} \left[\frac{1}{\pi} + 0.47 \left(N_{Re} \right)^{0.52} \right] . \tag{5}$$

In attempting to scale-up such types of equipment to commercial production, it is obvious that one would like to pack a large number of filaments or tubes into a large vessel and pass the reacting vapors continuously into and out of the unit. A model of such a commercial unit is shown in Figure 3. Transfer coefficients were measured for turbulent flow in this equipment under various conditions of flow and geometry.[8] The expression reproduced below was shown to be valid and was verified in pilot-plant operation:

$$k = \frac{D_v P}{d R T} \left(N_{Sc} \right)^{0.33} \left[\frac{1}{\pi} + 0.062 \left(N_{Re} \right)^{0.68 - 0.14 \, D_B} \right] \tag{6}$$

$$\left(d/D_B \right)^{0.50} \left(D_B/D_i \right)^{0.80} \left(D_B/L_B \right)^{1.39} \left(S_B/S_T \right)^{0.53} .$$

The effects of the operating variables and properties of the process materials upon deposition rates can be determined from this expression. Dimensions of the equipment enter into the expression in a straightforward manner with the exception of bulb diameter. Properties of the process materials enter in a less straightforward but not unduly complex manner.

This then completes the summary of all known published work on the evaluation of the transfer coefficient for diffusion during chemical vapor deposition.

FIGURE 2. CROSS FLOW UNIT FOR THE STUDY OF RATES OF DEPOSITION OF IODIDE TITANIUM
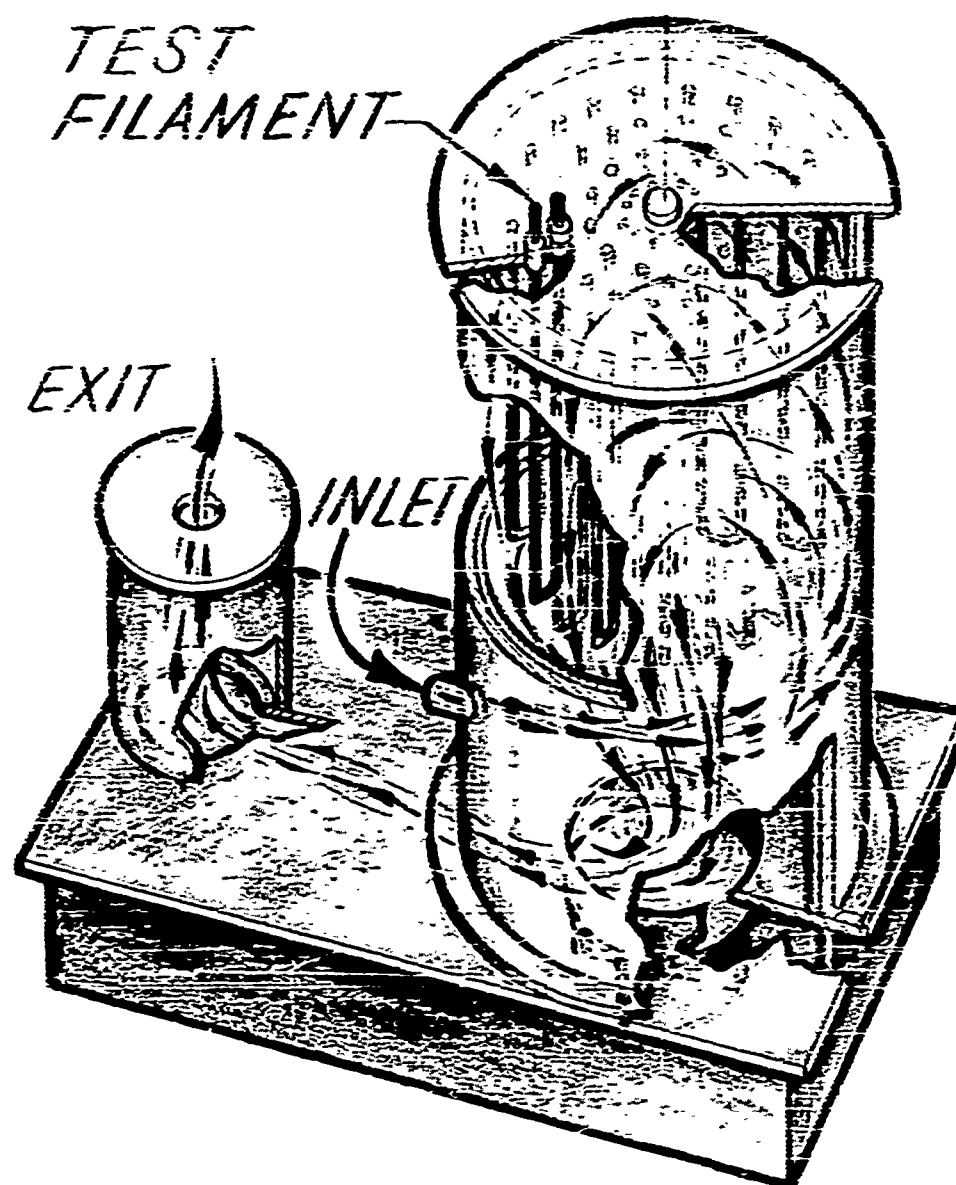
FIGURE 3. DETAILS OF MODEL OF COMMERCIAL DEPOSITION BULB

Evaluation of Effective Area

If Equation (2) is now re-examined, it can be seen that the next term to be evaluated in predicting deposition rates under diffusion control is the area term.

Again starting with the simplest case, for diffusion at a cylindrical surface of given radius (r_1) and length (L), the relationship shown in Equation (7) is applicable, this simply being the formula for the surface area of the cylinder:

$$A = 2\pi r_1 L \quad . \tag{7}$$

If the cylinder wall actually consists of a screen formed into a cylindrical tube, t. equation is multiplied by the screen porosity to obtain the proper area term.

For diffusion through an annular section, it has been demonstrated that the shape factor for heat transfer is also valid for deposition of zirconium from the tetraiodide, as shown in Equation (8)[9]:

$$A = \frac{2\pi L\,(r_2 - r_1)}{\ln r_2 / r_1} \quad . \tag{8}$$

Here the effect of radii takes a little more complicated form.

If the screen and the annular section are in series with the diffusion path, it has been shown that the relationship reproduced in Equation (9) should be employed[10]:

$$A = \frac{2\pi L\,(r_2 - r_1)}{\ln r_2 / r_1 + \delta / r_2 c} \quad . \tag{9}$$

The term $\delta / r_2 c$ has now been added to the previous area formula to include the effect of the screen resistance to diffusion.

Now reviewing the most complicated treatment of area evaluation, i. e., when the diffusion occurs through the screen and annular section in series flow and the inner radius of the annular surface (r_1) changes appreciably as a result of deposition (from r_{10} to r_{11}), the equation shown below has been derived and is applicable[10]:

$$A = \frac{\pi L Z\,(r_{11}^2 - r_{10}^2)}{(r_{11}^2 - r_{10}^2)\,(\ln r_2 + \delta / r_2 c + 1/2) + r_{10}^2 \ln r_{10} - r_{11}^2 \ln r_{11}} \quad . \tag{10}$$

The effect of this change in dimensions during the course of a production run has been ascertained for quite a few practical process situations. One such situation is shown in Figure 4. This is a schematic drawing of a typical iodide refining cell. The temperature of the deposition surface is higher than that of the crude feed, and as a result of this temperature gradient, a net transport of metal occurs. At the low temperature the metal feed is iodinated with free iodine. The metal iodide then diffuses to the hotter surface and pure metal is deposited and free iodine liberated. The iodine then diffuses back to again react with the feed.

DEPOSITED METAL

CRUDE FEED METAL

POROUS SCREEN
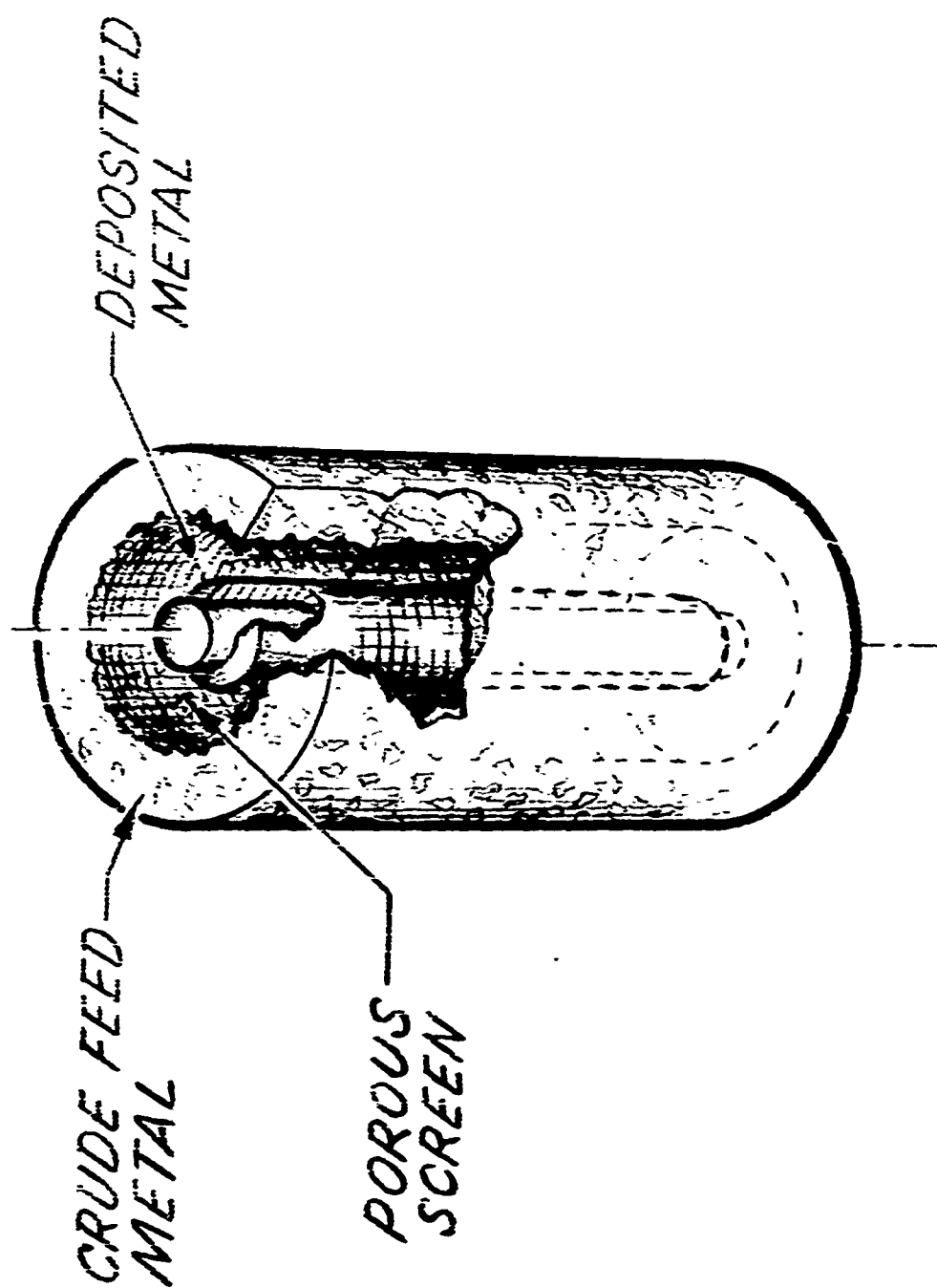
FIGURE 4. IODIDE DEPOSITION CELL

As shown in Figure 5, the average rate is therefore not only a function of the initial geometry, but, since the geometry changes during the run, as a result of metal deposition, the rate of deposition is also a function of the amount of metal deposited. Here, the average rate of deposition is shown as a function of initial surface diameter and the weight of metal produced. It can be seen that the average rate can vary by a factor of two in just this one type of iodide refining cell, simply due to the change in the dimensions of the deposition surface.

Evaluation of Diffusion Potential

Returning to Equation (2), it can be seen that the driving potential is the only other factor which needs to be evaluated for fixing the deposition rate. Equations for diffusion potentials were established for various types of diffusional processes many years ago.[5] The three cases which are presented in the next three equations are examples of this work for two-component systems.

In the case of diffusion through a stagnant film, a simple logarithmic driving force is applicable.

$$\Delta y = \ln \frac{(1 - y_2)}{(1 - y_1)} \ . \tag{11}$$

The diffusion potential for equal-molal counterdiffusion is:

$$\Delta y = y_1 - y_2. \tag{12}$$

Here, the driving force is simply the difference in mole fraction of the diffusing species between the surface and the bulk stream.

For nonequimolal counterdiffusion, where the ratio of molar flow in the two opposite directions is not unity, the correct form of the diffusion potential is shown in Equation (13):

$$\Delta y = \frac{1}{1 - x} \ \ln \frac{1 - (1 - x) (y_2)}{1 - (1 - x) (y_1)} \ . \tag{13}$$

In this case, the driving potential is not only a function of the mole fraction of the diffusing species, but also depends upon the ratio of the molar flow to and from the deposition surface.

Equilibrium limitations on concentrations have been pointed out by a number of investigators. As shown in Equation (14), the mole fraction (y) available for driving the diffusion process is generally lower than the actual mole fraction of the volatile metal compound (y'), due to the fact that the fractional equilibrium corrosion (E) can be appreciably less than unity:

$$y = E \ y' \ . \tag{14}$$
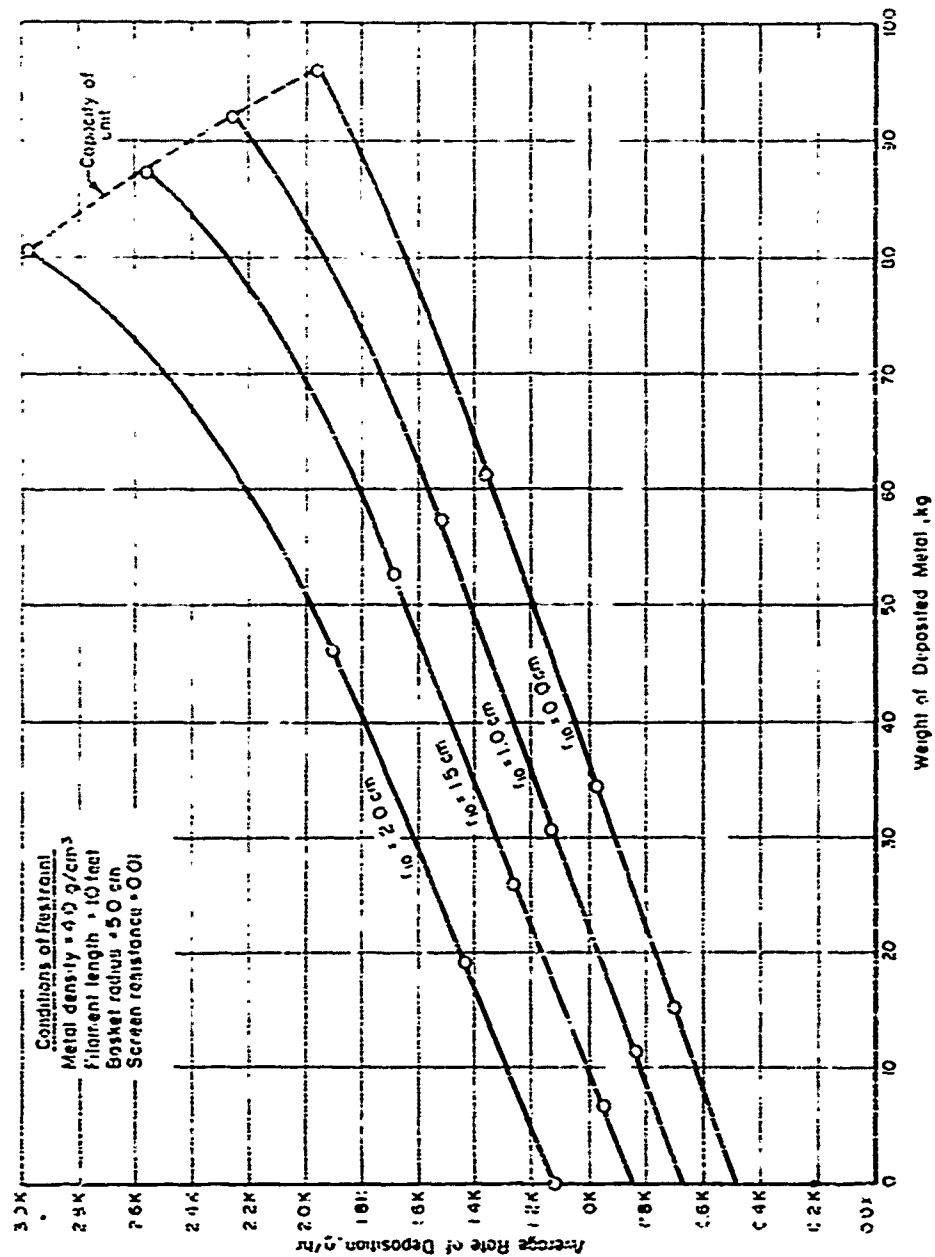
FIGURE 5. AVERAGE RATE OF DEPOSITION AS A FUNCTION OF WEIGHT OF DEPOSITED METAL.

The nature of this equilibrium correction is generally of complicated term. A number of years ago it was found that the apparent concentration for zirconium deposition from the iodide was of the form involving an arbitrary constant and the free energy of reaction.[11] Recently, this concept has been extended in a more complicated, semi-theoretical expression of the same general form to include the presence of zirconium diiodide by use of free energies (ΔG) of reaction[12]:

$$y = B e^{\frac{-\Delta G}{4RT}} (1 - 1.25 \, P_4^{1/4} \, e^{\frac{\Delta G - 2\Delta G'}{4RT}}) \ . \tag{15}$$

Equilibrium conditions also were thought to be encountered in published work on the decomposition of silicon tetraiodide to produce transistor-grade silicon.[13,15] The following equation shows how the fractional conversion (α) was empirically related to the iodide feed rate (F) and the reactor surface area (A):

$$\log F/A = 2.18 - \alpha/0.305 \ . \tag{16}$$

However, a reactant depletion mechanism could perhaps be better satisfied by such a relationship. In studies on the hydrogen reduction of columbium pentachloride in a fluidized bed, as the basis of a metallurgical process to produce columbium or to coat fuel nuclear fuel particles, correlation of data according to the linear relationship of Equation (17) has been established[16]:

$$\alpha = 1.474 - 0.0316 \, R_H + 0.0000360 \, R_H \, T - 0.001051 \, T \ . \tag{17}$$

This equation shows the fractional conversion (α) as a linear function of temperature (T) and excess hydrogen ratio (R_H). The conversion was also shown to be independent of gas preheat, bed particle size, and bed height over the range of conditions studied. This type of correlation suggests equilibrium behavior, but the actual situation has not yet been satisfactorily clarified.

Concentration depletion by reaction is generally encountered in all cases, and the flow pattern in the reactor must be known to evaluate the diffusion potential. In the case of complete mixing, the solution is quite simple, as shown in Equation (18):

$$y = \frac{M_w F - M_i W}{M_w F + (V - 1) M_i W} \ . \tag{18}$$

This type of correction for reactant depletion has been used for correlation of vapor-deposition rates under highly turbulent conditions in flow systems.

The effect of kinetic limitations on concentrations has been demonstrated in a recent study on the hydrogen reduction of molybdenum pentachloride in a flow system.[17] It was shown that the deposition process was apparently diffusion controlled, although it was not possible to identify the diffusing species. However, a number of expressions were derived to define the potential gradient when chemical-reaction rates were not negligible and included the effect of reactant depletion under conditions of piston flow through a cylindrical tube.

As an example of this work, for conditions in which molybdenum dichloride is the controlling species, the relationship shown in Equation (19) is reproduced:

$$r = \frac{k_4}{k_4 - AkRT/P} \ r_4^o \ \left[e^{-AkL/U} - e^{-k_4 PL/URT}\right] \ . \tag{19}$$

This equation shows the complex interrelationships between mass transfer and reaction rate in determining a potential gradient.

With this summary of published work on diffusion potentials, the task of predicting rates of deposition under conditions of diffusional control, within the limitations necessitated by the present state of our knowledge, is completed.

Problems Requiring Additional Research

Extension of present knowledge, not only in the area of fundamental studies on mechanisms but also measurements of the flow patterns and coefficients in models of various types of vapor-deposition systems, is obviously required.

Considerable effort is needed in the area of defining when natural convection effects become appreciable and how to interpret data under such circumstances. A large amount of study on reactions in surface boundary layers is being carried out in other fields, and this information should be modified and applied to the vapor-deposition field. A great deal of information also needs to be developed in the transfer problems associated with coating complex-shaped objects, since these are frequently of commercial interest.

Little is known about the effects of scale and intensity of turbulence in vapor-deposition systems, i.e. how are the over-all rate and uniformity of deposition affected by both natural and artificially induced turbulence. For instance, studies on the application of sonic energy to vapor-deposition systems is certainly warranted.

Fluidized-bed vapor-deposition processes have received unusual attention during the past few years from both industrial and Government laboratories for numerous applications. However, little is known about the reaction and flow mechanisms in such equipment. The scale-up problems in these units, particularly when two or more feed streams cannot be mixed before they are injected into the fluidized bed, are indeed formidable. Use of the plasma jet as a chemical reactor is also rapidly breaking away from the curiosity stage. Information on the turbulent diffusion coefficients in the jet would be of considerable help in guiding process work based on vapor-deposition reactions in this type of reactor.

It should be obvious that the potential of the vapor-deposition techniques is enormous, but further large-scale commercialization will have to be based on fundamental considerations.

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Nomenclature

A — area for diffusion, ft^2

a — exponent on surface area term

B — a constant, independent of temperature

d — cylinder or filament diameter, ft

D_B — bulb diameter, ft

D_i — inlet diameter, ft

D_v — diffusivity, ft^2/hr

E — fractional conversion at equilibrium

E_i — activation energy, kcal/g-mole

e — a constant, 2.718

F — feed rate, lb/hr

G — free energy, kcal/g-mole

k — mass-transfer coefficient, lb-mole/(hr)(ft^2)

k_3 — reaction rate constant for carbon deposition, $\text{lb-K}/(\text{atm})^n(ft^2)^{a+1}(hr)$

k_4 — reaction rate constant for molybdenum pentachloride reduction, ft^3/lb-mole/hr

L — length of reaction surface or conduit, ft.

M_w — molecular weight of deposit, lb/lb-mole or

M_f — molecular weight of feed, lb/lb-mole

N_{Re} — Reynolds number of system

N_{Sc} — Schmidt number of gas

n — partial-pressure exponent

P — total pressure, atm

P_2 — partial pressure of zirconium tetraiodide, atm

P_1 — partial pressure of hydrocarbon, atm

R — gas constant, atm-ft^3/lb-mole-K, or kcal/g-mole-K

k_H — excess hydrogen ratio

r_1 — radius of a cylindrical deposition surface, ft

r_2 — outer radius of an annular section, ft

r_{10} — initial radius of a cylindrical deposition surface, ft

r_{11} — final radius of a cylindrical deposition surface, ft

S — surface area of particles, ft^2

S_B — surface area of bulb, ft^2

S_T — total surface area, ft^2

t — system temperature, K

U — flow velocity, ft/hr

V — increase in moles of gas per mole of feed as a result of reaction

W — rate of deposition, lb/hr

x — ratio of molar flow rates

y — effective mole fraction of diffusing component

y' — actual mole fraction of diffusing component

y_1 — mole fraction of molybdenum pentachloride

z — distance through which diffusion occurs, ft

— fractional conversion of feed

Δy — diffusion potential

δ — thickness of porous screen, ft

— porosity of screen

π — a constant, 3.142

ln — natural logarithm

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